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Engineer Research and  
Development Center

# **Draft Protocol for Evaluating, Selecting, and Implementing Monitored Natural Attenuation at Explosives-Contaminated Sites**

*by Judith C. Pennington, Richard Bowen, James M. Brannon, Mansour Zakikhani,  
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# Contents

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Preface .....	vi
List of Acronyms .....	viii
1—Introduction .....	1
Purpose of this Document .....	1
Background .....	2
Monitored Natural Attenuation .....	4
2—Natural Attenuation as a Remedial Alternative .....	6
Conceptual Framework .....	6
Transformation of TNT .....	7
Transformation of RDX .....	8
Immobilization of TNT .....	9
Immobilization of RDX .....	10
Biodegradation of TNT .....	10
Biodegradation of RDX .....	13
Advantages and Limitations .....	13
Remedial Alternative Selection Process .....	14
Federal policy and guidance .....	17
State policy and guidance .....	24
Monitored natural attenuation of nonexplosives contaminants .....	26
Applications of Natural Attenuation .....	28
Summary .....	28
3—Protocol for Evaluation, Selection, and Implementation of Monitored Natural Attenuation as a Remedial Alternative .....	31
Scope of the Protocol .....	31
Regulatory Coordination .....	32
Procedure .....	34
Evaluation of monitored natural attenuation as a remedial alternative .....	34
Comparison of monitored natural attenuation to other remedial alternatives .....	34
Considerations for implementing monitored natural attenuation .....	40
Step 1. Evaluate adequacy of existing data for development of a preliminary conceptual model of the site .....	40

Step 2. Evaluate existing data and conceptual model for evidence of natural attenuation .....	45
Step 3. Develop numerical model(s) .....	47
Step 4. Collect additional data specific to natural attenuation of explosives .....	50
Step 5. Inform stakeholders and coordinate further evaluation .....	58
Step 6. Refine the site conceptual and numerical models .....	60
Step 7. Assess feasibility of monitored natural attenuation .....	60
Step 8. Evaluate protectiveness of monitored natural attenuation for human health and the environment .....	61
Step 9. Compare monitored natural attenuation to other alternatives using established evaluation criteria .....	62
Step 10. Finalize long-term monitoring and contingency plans .....	63
References .....	68
Appendix A: Microbial Degradation Potential .....	A1
Appendix B: Louisiana Army Ammunition Plant .....	B1
Appendix C: Model References and Sources .....	C1
Appendix D: Groundwater Modeling at Louisiana Army Ammunition Plant .....	D1
Appendix E: Statistics .....	E1
Appendix F: Interim Army Policy on Natural Attenuation for Environmental Restoration .....	F1
Appendix G: Points of Contact .....	G1
SF 298	

## List of Figures

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Figure 1. Biotransformation of TNT under thermophilic compost conditions .....	8
Figure 2. Structural representation of TNT, TNT transformation products, RDX, and several other explosives/propellants .....	9
Figure 3. Reaction of TNT transformation product 2,4-diamino-6-nitrotoluene with functional groups of soil organic matter to yield hydrolysable, partially hydrolysable, and nonhydrolysable products .....	11
Figure 4. Comparison of CERCLA/RCRA action processes .....	15
Figure 5. Remedial action evaluation process .....	16
Figure 6. Alternative development and screening .....	18
Figure 7. Detailed analysis of alternatives .....	19

Figure 8.	Relationship between screening criteria and detailed evaluation .....	20
Figure 9.	Flowchart for intrinsic remediation of fuel hydrocarbons .....	27
Figure 10.	Flowchart to evaluate and implement natural attenuation at sites contaminated with chlorinated solvents .....	29
Figure 11.	Protocol for monitored natural attenuation of explosives .....	35
Figure 12.	Idealized groundwater monitoring well network for monitoring natural attenuation .....	65

## List of Tables

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Table 1.	CERCLA/RCRA Terminology .....	16
Table 2.	Summary of EPA Policy for the Evaluation of Monitored Natural Attenuation as a Remedial Alternative .....	23
Table 3.	Summary of Findings of State Regulatory Agency Interviews Regarding Monitored Natural Attenuation .....	25
Table 4.	Potential Advantages and Disadvantages of Monitored Natural Attenuation Remedial Alternative .....	30
Table 5.	Factors Favoring Selection of Monitored Natural Attenuation as a Remedial Alternative .....	30
Table 6.	Information and Data-Gathering Example and Data Relevance .....	41
Table 7.	Site Characterization Data .....	42
Table 8.	Qualitative Input to the Preliminary Conceptual Model and Examples .....	43
Table 9.	Quantitative Input to Conceptual Model and Examples .....	43
Table 10.	Data Collection Information Sources .....	46
Table 11.	Equations Used to Rapidly Assess Chemical Fate and Transport .....	48
Table 12.	Soil Characteristics That Regulate Microbial Habitat .....	56
Table 13.	Exposure Evaluation Factors .....	62
Table 14.	Criteria for Detailed Analysis of Monitored Natural Attenuation .....	63

# Preface

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This protocol was prepared jointly by Arthur D. Little, Inc. (ADL), Cambridge, MA, and the U.S. Army Engineer Research and Development Center (ERDC) Environmental Laboratory (EL) and Geotechnical Laboratory (GL) both of Vicksburg, MS, and U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), Hanover, NH. Development of the protocol was funded under Project 9518 by the Environmental Security Technology Certification Program (ESTCP), Dr. Jeffrey Marqusee, Director, and under Project 1043 by the Strategic Environmental Research and Development Program (SERDP), Dr. John Harrison and Mr. Bradley P. Smith, Executive Directors. The U.S. Army Industrial Operations Command, Mr. Cyril Onewokae, Environmental Quality Directorate, Rock Island, IL, funded monitoring at the validation site.

The ADL contributors included Mr. Richard Bowen, Ms. Janet Mahannah, and Mr. Scot Gnewuch, Senior Consultants of the Environmental Science and Technology Practice of Arthur D. Little, Inc.

The ERDC contributors included Drs. Judith C. Pennington, Douglas Gunnison, and James M. Brannon, Ecosystem Processes and Effects Branch, Dr. Mansour Zakikhani, Water Quality and Contaminant Modeling Branch (WQCMB), and Ms. Joan Clarke, Fate and Effects Branch, Environmental Processes and Effects Division (EPED), EL, and Mr. Danny W. Harrelson, Engineering Geology Branch (EGB), Earthquake Engineering and Geosciences Division (EEGD), GL. The protocol was prepared under the direct supervision of Drs. Mark S. Dortch, Chief, WQCMB, and Lillian D. Wakeley, Chief, EGB, and under the general supervision of Dr. Richard E. Price, Chief, EPED, Dr. Arley G. Franklin, Chief, EEGD, Dr. John Harrison (retired), Director, EL, and Dr. William F. Marcuson III, Director, GL. The CRREL contributor was Dr. Thomas F. Jenkins.

The authors acknowledge the advice of the following members of the Technical Review Committee for Natural Attenuation of Explosives: Mr. Michael Barden, Geosciences Resources, Ltd., Albuquerque, NM, formerly of Wisconsin Department of Natural Resources, Madison, WI; Mr. Patrick Haas, U.S. Air Force Center for Environmental Excellence, San Antonio, TX; Mrs. Laurie Haines, U.S. Army Environmental Center (AEC), Aberdeen Proving Ground, MD; and Dr. David C. White, University of Tennessee, Knoxville, TN.



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At the time of publication of this report, Dr. Lewis E. Link was Acting Director of ERDC, and COL Robin R. Cababa, EN, was Commander.

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# List of Acronyms

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AFCEE	Air Force Center for Environmental Excellence
ARAR	Applicable or Relevant and Appropriate Requirement
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DoD	Department of Defense
EPA	Environmental Protection Agency
ERDC	Engineer Research and Development Center
FS	Feasibility Study
LAAP	Louisiana Army Ammunition Plant
LUST	Leaking Underground Storage Tank
NCP	National Contingency Plan
NPL	National Priorities List
OSWER	USEPA Office of Solid Waste and Emergency Response
PA	Preliminary Assessment
RA	Risk Assessment
RCRA	Resource Conservation and Recovery Act
RDX	Royal Demolition Explosive (Hexahydro-1,3,5-trinitro-1,3,5-triazine)
RI	Remedial Investigation

ROD	Record of Decision
RFA	RCRA Facility Assessment
RFI	RCRA Facility Investigation
RTDF	Remedial Technologies Development Forum
SI	Site Investigation
SIAD	Sierra Army Depot
TCE	Trichloroethene
TNT	2,4,6-Trinitrotoluene
USAEC	U.S. Army Environmental Center
UST	Underground Storage Tank
VOC	Volatile Organic Compound
WES	Waterways Experiment Station

# 1 Introduction

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## Purpose of this Document

This document has been prepared to integrate available data into guidance that can be used to advise and assist Department of Defense (DoD) installations as they assess the feasibility of and/or implement monitored natural attenuation as a remedial alternative for sites contaminated with the explosives TNT (2,4,6-trinitrotoluene), its transformation products, and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine). Procedures set forth in this document are intended to aid in determining whether natural attenuation processes are sufficient to protect human health and the environment by meeting remediation goals within a reasonable time frame.

The document includes a review of the remedial alternatives selection process to provide a context into which monitored natural attenuation as a remedial alternative for explosives can be integrated. This review includes relevant regulatory and technical perspectives that should be useful to installation environmental managers and their contractors. The selection and implementation procedure is outlined and described in a series of steps that are conceptualized in a flowchart. The procedure embodies an iterative process designed to lead to a weight-of-evidence for monitored natural attenuation of explosives as a viable remedial alternative at specific sites. The steps of the protocol are supported with technical appendixes based upon data accumulated at the Louisiana Army Ammunition Plant (LAAP), Minden, LA. Appendixes also include references to (a) more detailed technical data for the LAAP demonstration (Appendixes A, B, and D), (b) groundwater models and sources of groundwater models (Appendix C), (c) statistics (Appendix E), (d) interim Army policy (Appendix F), and (e) points of contact for supporting information (Appendix G). These appendixes may be of use to engineers and scientists and/or site managers and contractors who must accumulate and assess site data.

**Purpose of Document**

- ⇒ Integrate data relating to monitored natural attenuation of explosives in environmental media
- ⇒ Provide step-by-step protocol to assist Army installations in considering, evaluating, and/or implementing monitored natural attenuation as a remedy for sites contaminated with explosives

**Functions of Document**

- ⇒ Initial screening of feasibility of monitored natural attenuation as a remedial alternative
- ⇒ Development of evidence supporting the selection of monitored natural attenuation as a remedial alternative
- ⇒ Selection of monitored natural attenuation as a remedial approach
- ⇒ Implementation of monitored natural attenuation as a remedial approach

**Intended Users of Document**

- ⇒ Installation environmental managers
- ⇒ Site contractors
- ⇒ Cleanup program managers

**Other**

- ⇒ References to supporting documents
- ⇒ Points of contact

## **Background**

Federal, State, and local environmental protection and public health laws require that the DoD reduce or eliminate the environmental and health impacts resulting from current and past defense facilities operations. In response, the services have implemented active programs to address four fundamental areas of environmental focus: pollution prevention, cleanup, compliance, and conservation.

Cleanup involves the environmental remediation of soil, sediment, ground-water, surface water, and structures contaminated with hazardous and toxic materials from past military activities. Cleanup in this context includes both mass removal and risk reduction. The cost to complete the DoD cleanup program is estimated to be over \$35 billion using traditional approaches that may

not provide long-term protection or cost-effective solutions.<sup>1</sup> To address long-term protection needs and cost-effectiveness, cleanup alternatives are actively being pursued by DoD services (Army, Navy, Air Force) and others involved in the field of environmental protection.

That the environment has some capacity to naturally alter and assimilate natural and anthropogenic contaminants without unacceptable impacts has long been recognized. This capacity to alter and assimilate contaminants is proposed as an acceptable means of protecting the public health and environment while reducing the cost of site remediation. In fact, the National Contingency Plan (NCP) now requires that natural attenuation be considered as a potentially acceptable remediation alternative (*Federal Register* 1990a).

In response to the recognition that monitored natural attenuation may provide a realistic, protective, and cost-effective solution for the cleanup of some contaminated sites, extensive efforts have focused on evaluating the potential for natural attenuation and developing various degrees of technical guidance to incorporate natural attenuation into the evaluation, selection, and implementation of remedial alternatives. Thus far, guidance has been developed or proposed for application to sites contaminated with petroleum hydrocarbons (Wiedemeier et al. 1995) and chlorinated organics (Remediation Technologies Development Forum (RTDF) 1996; EPA 1998).

The Army is the DoD single service manager for explosives and as such has been responsible for the management of munitions throughout their entire life cycle—from development and manufacture through disposal. Consequently, the Army has the lead for addressing needs for the treatment of explosives-contaminated wastes, including the cleanup of sites contaminated with explosives. Due to the uniqueness of these contaminants, these sites present a special set of problems to the environmental manager, including site investigation/ characterization, environmental fate and effects, and treatment.

Under the joint sponsorship of the Environmental Security Technology Certification Program and the Strategic Environmental Research and Development Program, a 2-year demonstration of monitored natural attenuation was performed at the Louisiana Army Ammunition Plant, Minden, LA (Pennington et al. 1999a,b; Pennington, Zakikhani, and Harrelson 1999). Results of that study and a smaller study at Joliet Army Ammunition Plant, Wilmington, IL, sponsored by the Industrial Operations Command (reported in Pennington et al. 1998a) contributed to development of this protocol. Points of contact for the two studies are given in Appendix G.

This report has been prepared to address the specific needs for considering monitored natural attenuation as a potential remedial action at sites contaminated with explosives.

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<sup>1</sup> Unpublished Material, 1995, John Cullinane, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

## Monitored Natural Attenuation

Monitored natural attenuation as a remedial alternative (also known as passive remediation, natural restoration, and intrinsic bioremediation) can be defined as the reduction of contaminant concentrations to environmentally benign levels through natural processes. These natural processes include, but are not limited to, abiotic and biotic transformation (mineralization and degradation), sorption/ desorption, ion exchange, and complexation. Many in the environmental field tend to limit monitored natural attenuation in the subsurface to biodegradation of contaminants which limit its application of monitored natural attenuation to organic, readily biodegradable contaminants. However, inorganic contaminants or less readily biodegradable organic contaminants may be affected by other processes, such as immobilization, that provide for natural attenuation in accordance with the definition presented above.

That the environment can withstand significant acute or chronic contaminant loadings without exhibiting adverse consequences has long been recognized. As the natural diminishing of contaminant concentrations over time was initially being documented, the term "passive remediation" was most often used. The process was recognized to occur beneath unlined lagoons and landfills and was recognized as due primarily to advection and diffusion. Metals and other inorganic constituents were monitored in the groundwater beneath these surface impoundments, and the plumes behaved according to classic advection and diffusion theory.

Later, technical data indicated that released contaminants were subject to much more than simple dilution. With the growth in understanding of naturally occurring processes such as biodegradation that affect the behavior of contaminants in the subsurface, the fact that many of these processes can contribute to a reduction in concentration and mass of contaminants without human intervention has been recognized. In some cases, this reduction in concentration and mass is sufficient to warrant consideration of monitored natural attenuation of contaminants as a viable remedial alternative.

With the growth in understanding of natural processes, monitored natural attenuation is being increasingly recognized as a viable remedial alternative subject to the same screening criteria as active remedial alternatives, rather than simply being an interesting aspect of uncontrolled contamination. A growing experience and database are further supporting the consideration of natural attenuation as a remedial alternative. However, the experience and data are primarily related to the attenuation of petroleum hydrocarbons and organic solvents.

The technical and implementation aspects of monitored natural attenuation as a remedial action for military-unique contaminants, such as explosives, are currently being assessed by the U.S. Army Engineer Research and Development Center (ERDC). Evaluating the feasibility of monitored natural attenuation for

explosives-contaminated sites is affected by several factors that distinguish such sites from those contaminated with solvents or petroleum hydrocarbons. For example, explosives degrade less rapidly and tend to be less mobile than solvents or petroleum hydrocarbons.

A project to develop tools that can be used to assess the potential for monitored natural attenuation of explosives as a remedial alternative has been conducted at the ERDC. The technical objectives of this program included the following:

- a.* Develop microbial monitoring tools.
- b.* Determine the feasibility of using stable isotopes to monitor natural attenuation of explosives.
- c.* Identify hydrogeological and geochemical characteristics that may be used to determine the rate and extent of natural attenuation.
- d.* Conduct mass balance studies to provide input to groundwater models.
- e.* Develop subsurface models specifically applicable to biogeochemical transport processes influencing contaminant concentrations in the subsurface.

This work was conducted at the ERDC and in the field at Louisiana Army Ammunition Plant, one of the most extensively studied explosive-contaminated Army sites.



## **2 Natural Attenuation as a Remedial Alternative**

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### **Conceptual Framework**

For monitored natural attenuation to function as a remedial alternative for explosives-contaminated sites, the natural fate processes of explosives must be demonstrated to provide reduction in contaminant mass over time. Furthermore, the reduction in mass must occur at a rate sufficient to reduce the risk to potential receptors.

The applicability of monitored natural attenuation as a remedial alternative is dependent in part on site-specific characteristics that affect the spread of contamination, the potential for future exposures, and the remedial goals. To address these issues, adequate site characterizations involving physical, environmental, and hydrogeological assessments are required. A second factor in determining the applicability of monitored natural attenuation as a remedial alternative is a requirement for the accurate prediction and demonstration of its effectiveness. This latter factor requires the examination of contaminant characteristics (e.g., type and concentration), mechanisms involved in contaminant attenuation, and environmental factors that affect contaminant attenuation.

Although required for selection of any remedial alternative, characterization of site hydrology and geology plays a particularly critical role in the use of monitored natural attenuation as a remedial alternative. Of special relevancy are groundwater flow rate and direction, lateral and vertical extent of contamination, hydraulic conductivity and recharge rate, and the nature of subsurface geology. Attenuation processes must be demonstrated to occur faster than the site hydrologic regime can carry contaminants to potential receptors.

Explosives contamination frequently consists of several different chemical compounds. Consequently, attenuation mechanisms depend upon the behavior of the specific explosive in the soil and aquifer. The focus of this protocol is on the two most widespread explosives contaminants, TNT and RDX, and their potential degradation products.

TNT and RDX are subject to several environmental fate processes that may result in attenuation and reduction in the mass of contaminant in the subsurface. These processes are transformation, immobilization, and biodegradation.

## Transformation of TNT

Environmental transformation of TNT is a significant fate process for two reasons. First, the transformation products may be as undesirable as TNT because of toxicity and/or mutagenicity (Jarvis, McFarland, and Honeycutt 1998; Honeycutt, Jarvis, and McFarland 1996; Griest et al. 1993; Tan et al. 1992; Won, DiSalvo, and Ng 1976). Second, the transformation products have the potential for immobilization reactions with soil components (Pennington et al. 1997, 1998b, and in preparation (Explosives Conjugation Products in Remediation Matrices: Final Report); Thorn 1997). Transformation of TNT generally results from abiotic or cometabolic microbial reduction of one or more of the three nitro groups to amines resulting in new products with different properties and the potential for further reactions (Dawel et al. 1997; Li et al. 1997; Pasti-Grigsby et al. 1996; Thorn 1997; Daun et al. 1998; Figure 1 from Kaplan and Kaplan 1982). Both abiotic and cometabolic microbial reduction typically produces the same products. These include 4-amino-2,6-dinitrotoluene (4ADNT), 2-amino-4,6-dinitrotoluene (2ADNT), 2,4-diamino-6-nitrotoluene (2,4DANT), and 2,4,6-triaminotoluene (TAT) (Figure 2). Other products identified in laboratory systems include 2-hydroxylamino-4,6-dinitrotoluene (2HADNT) and 4-hydroxylamino-2,6-dinitrotoluene (4HADNT), which are unstable intermediates that have been observed in compost (Kaplan and Kaplan 1982) and bioslurry treatment systems (Daun et al. 1998), 4,N-acetylamino-2-amino-6-nitrotoluene produced under aerobic conditions in soil columns (Bruns-Nagel et al. 1996), a hydride-Meisenheimer complex in microbial enrichment cultures (Vorbeck et al. 1994, 1998; French, Nicklin, and Bruce 1998), and azoxytoluenes (Kaplan and Kaplan 1982; Hawari et al. 1998). The transformation products 4ADNT and 2ADNT are often observed in TNT-contaminated groundwater (Pennington et al. 1999a,b; Pennington, Zakikhani, and Harrelson 1999). Their presence is evidence of a transformation mechanism. These two monoamino transformation products are produced abiotically under a wide range of pH (5 to 7) and oxidation/reduction conditions (+500 mV to -150 mV) (Brannon, Price, and Hayes 1998). Moderate (0 mV) to extreme (-150 mV) reducing conditions are required to produce the diamino transformation products. However, under strongly reducing conditions (-150 mV), these products do not remain in solution, but become associated with the soil solid phase (see "Immobilization of TNT" below). Extremely reducing conditions (-200 mV) are required to produce the highly reactive 2,4,6-triaminotoluene, which is unlikely to be observed in groundwater (Funk et al. 1993; Lenke et al. 1994; Preuss and Rieger 1995; Lewis et al. 1996). The monoamino transformation products are the products most likely to be observed in groundwater.

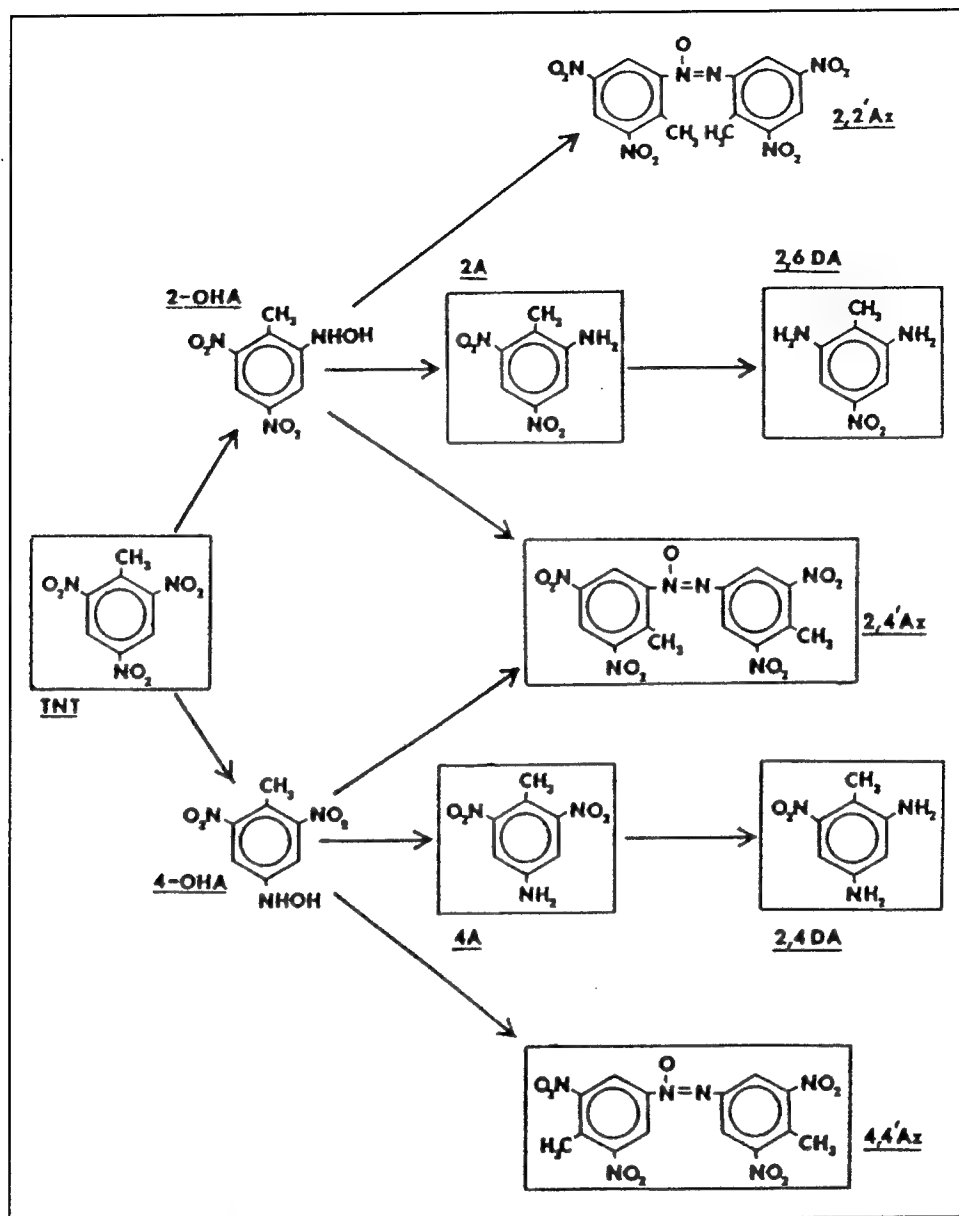


Figure 1. Biotransformation of TNT under thermophilic compost conditions (Kaplan and Kaplan 1982)

### Transformation of RDX

Transformation products of RDX include mono-, di-, and tri-nitroso derivatives (McCormick, Cornell, and Kaplan 1981). These products are rarely observed in soil or groundwater, but have been observed in laboratory microcosms (Pennington et al. 1999a,b; Price, Brannon, and Yost 1998). RDX nitroso derivatives are formed more readily under aerobic than under anaerobic conditions. Under anaerobic conditions, the nitroso derivatives are quickly mineralized (Price, Brannon, and Yost 1998).

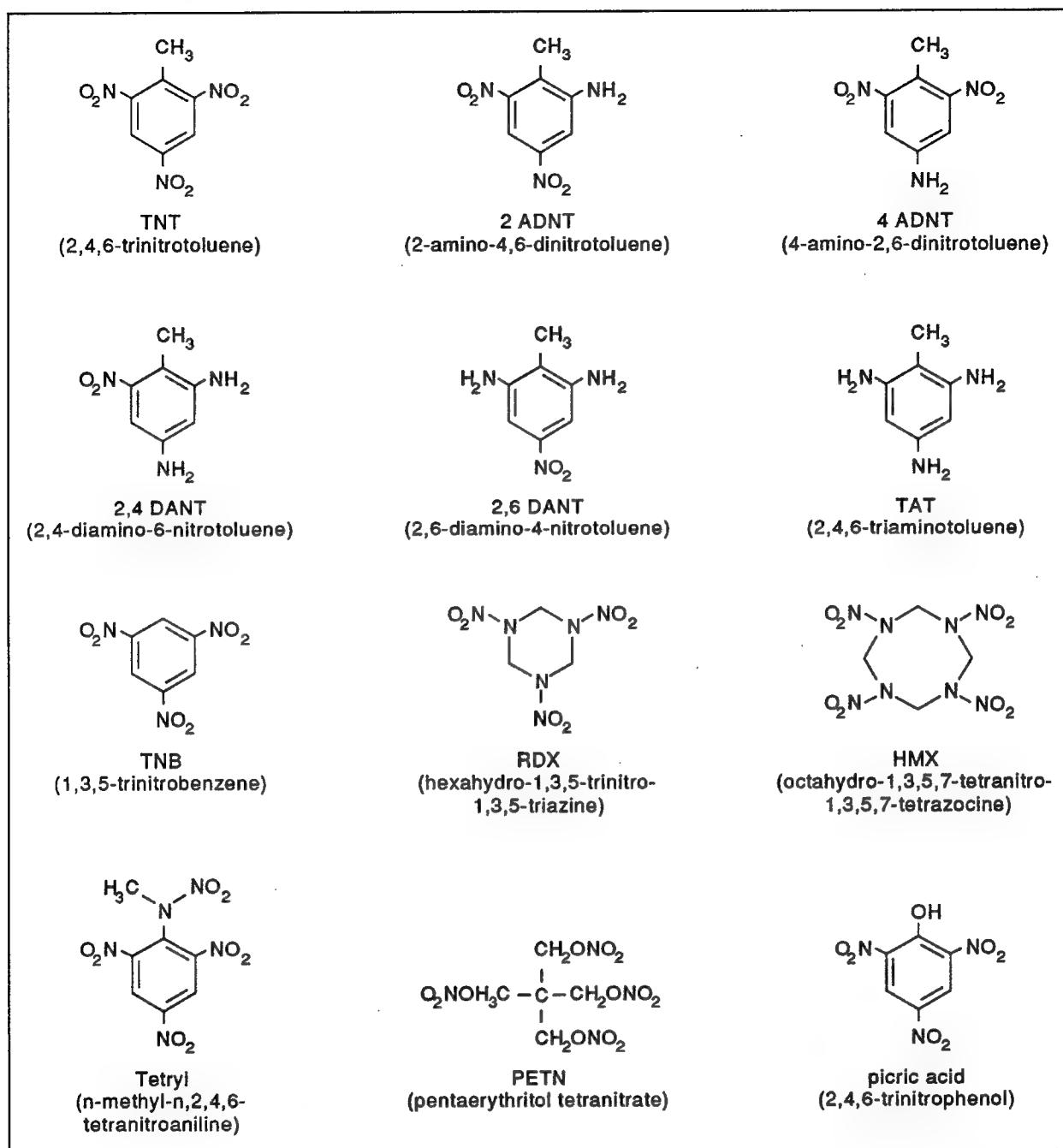


Figure 2. Structural representation of TNT, TNT transformation products, RDX, and several other explosives/propellants

### Immobilization of TNT

Immobilization occurs because the aminated transformation products of TNT have the potential to react with certain functional groups on soil organic carbon (Dawel et al. 1997; Thorn 1997; Pennington et al. 1995, 1998b, in preparation (Explosives Conjugation Products in Remediation Matrices: Final Report);

Haderlein and Schwarzenbach 1995) (Figure 3). These reactions are much more favorable for TNT than for RDX (Price, Brannon, and Hayes 1997; Price, Brannon, and Yost 1998). The products of TNT reactions with organic carbon are not very soluble and are resistant to chemical hydrolysis (Thorne and Leggett 1997) and microbial degradation (Pennington et al. 1997, 1998b, in preparation (Explosives Conjugation Products in Remediation Matrices: Final Report); Daun et al. 1998; Lenke et al. 1998). Limited solubility reduces the potential for migration of these products through the soil and for availability to plants and animals. Since organic carbon levels tend to decline with soil depth, the potential for immobilization is much greater in surface than in aquifer soils. Immobilization of TNT is greater under reduced than under oxidized conditions (Price, Brannon, and Hayes 1997). Formation of electron donor-acceptor complexes by reactions between clay minerals and TNT can also increase retention of TNT in aquifers (Haderlein and Schwarzenbach 1995). The site potential for immobilization of TNT must be estimated indirectly from loss of contaminant mass, including loss of transformation products, over time as determined by a carefully executed groundwater monitoring program. Other indicators of immobilization potential are the presence of TNT transformation products, organic carbon, and reduced iron in groundwater. Adequate tests for directly measuring immobilization in situ are not currently available; however, batch shake and column tests using aquifer soils can provide indirect evidence.

### **Immobilization of RDX**

Current evidence suggests limited potential for immobilization reactions of RDX. In compost experiments, decreases in extractable RDX after 20 days were significantly smaller than decreases in extractable TNT, which suggests that RDX is not extensively immobilized even in a high organic carbon matrix (Pennington et al. 1995). Groundwater data from Cornhuskers Army Ammunition Plant also suggest much less immobilization of RDX than of TNT since the extent of the RDX plume exceeds the TNT plume (Kipp et al. 1996). Although definitive data concerning the potential extent of immobilization of RDX and its transformation or degradation products are not currently available, Step 3 of this protocol includes a description of tests for evaluating the potential for adsorption and transformation that include potential for immobilization (see Chapter 3 of this report).

### **Biodegradation of TNT**

Two proposed pathways for microbial mineralization of TNT include degradation of TAT (Rieger and Knackmuss 1995; Funk et al. 1993; Pruess and Rieger 1995; Crawford 1995) and sequential removal of nitro groups to produce toluene which is subsequently degraded (Duque et al. 1993). Although biodegradation of TNT and its aminated transformation products occurs under a wide range of environmental conditions, the rate is extremely slow (Pennington et al. 1999a,b; Price, Brannon, and Hayes 1997). Because of the slow rate, simple mineralization products of TNT do not tend to accumulate in measurable

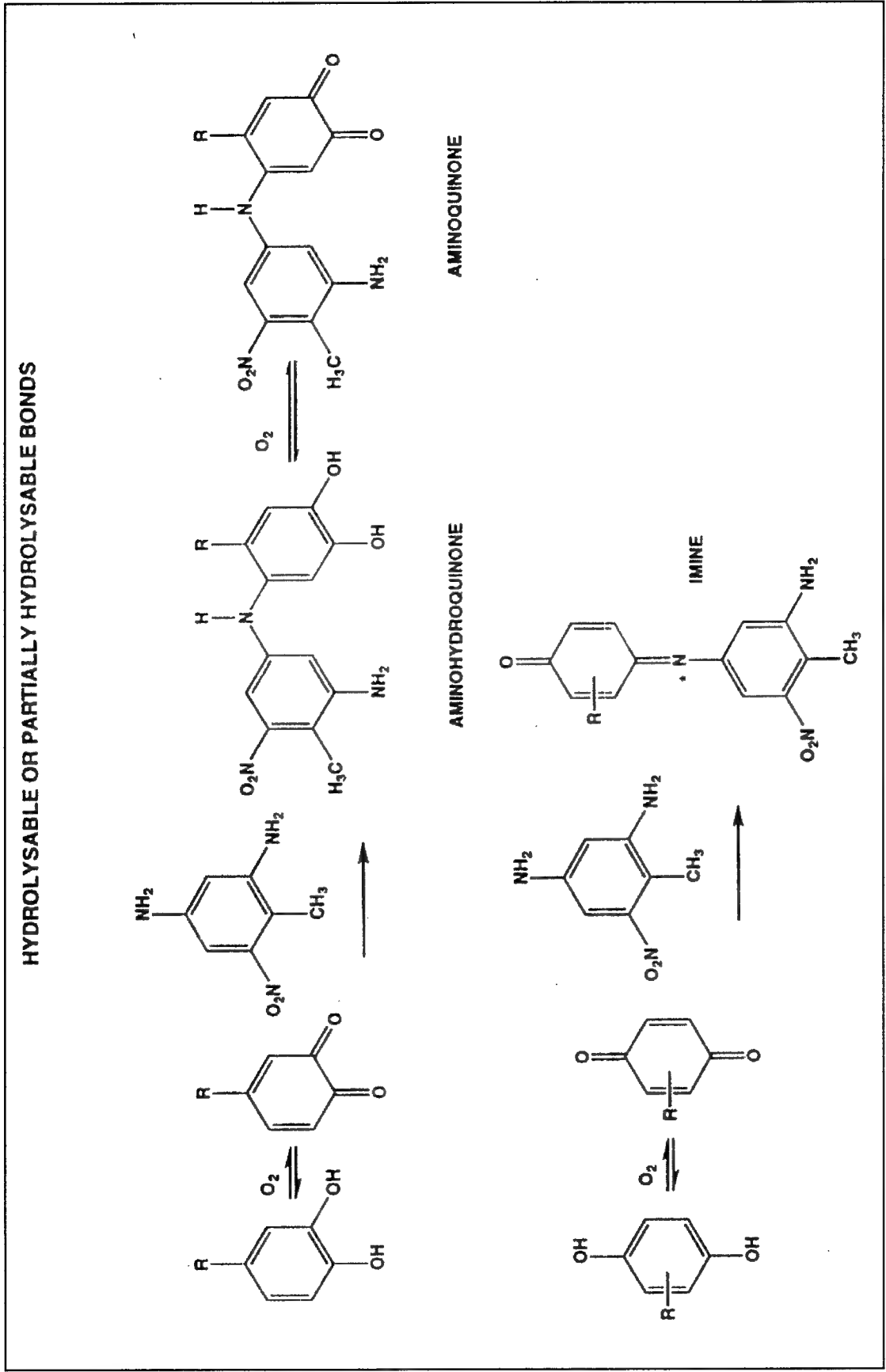


Figure 3. Reactions of TNT transformation product 2,4-diamino-6-nitrobenzene with functional groups of soil organic matter to yield hydrolysable (aminohydroquinone and aminoquinone), partially hydrolysable (imine), and nonhydrolysable (heterocyclic) products (Pennington et al. 1998b) (continued)

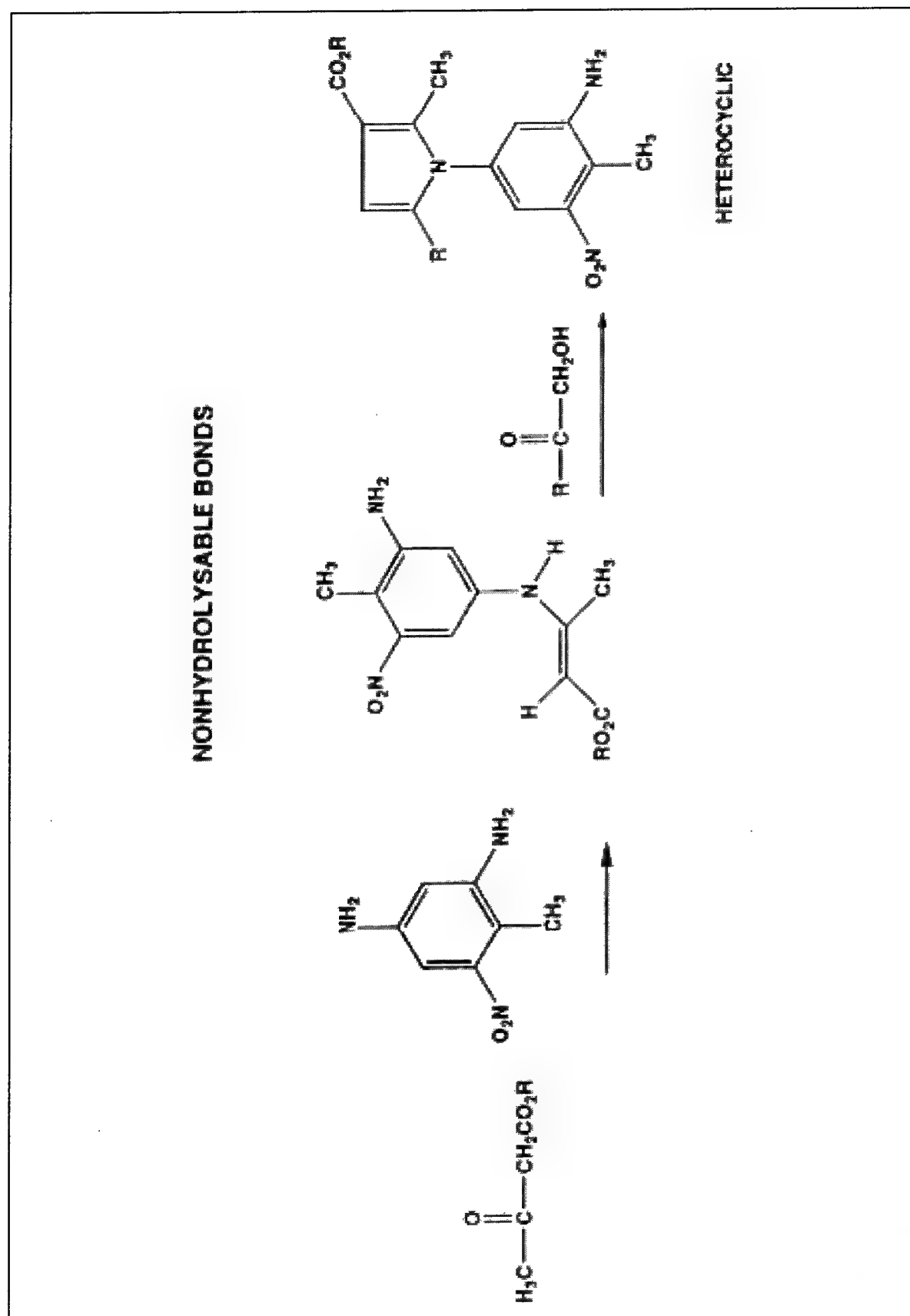


Figure 3. (Concluded)

quantities in groundwater (Pennington et al. 1999a,b). Therefore, geochemical evidence of mineralization, such as accumulation of methane, is elusive.

### **Biodegradation of RDX**

In natural systems, RDX is subject to mineralization at a faster rate than TNT, but the rate is still relatively slow. Under anaerobic conditions, RDX mineralization is favored and potentially yields several nitroso and nitramine intermediates and, ultimately, hydrazines and methanol (McCormick, Cornell, and Kaplan 1981, 1985; Regan and Crawford 1994; Funk et al. 1993). Aerobic biodegradation has also been observed in the laboratory with enrichment cultures from RDX-contaminated soils (Coleman, Nelson, and Duxburg 1998; Binks, Nicklin, and Bruce 1995; Yang et al. 1983). RDX mineralization in soil and groundwater requires sufficient cosubstrate, microbial nutrients, and sufficient populations of mineralizing microbes (Pennington et al. 1999a,b; Price, Brannon, and Yost 1998). The potential for mineralization in site soils can be measured with the microbial degradation potential tests described in Appendix A of this report.

### **Advantages and Limitations**

The greatest advantage of monitored natural attenuation over engineered remedial alternatives is the potential cost savings. In a cost comparison with two other technologies, in situ bioremediation and activated carbon adsorption, estimated cost savings by use of monitored natural attenuation were significant (Pennington, Zakikhani, and Harrelson 1999). Monitored natural attenuation also generates less waste, reduces the risk of human and environmental exposure to contaminants during remediation, and is less intrusive than other remedial alternatives. Procedures for implementing monitored natural attenuation, i.e., procedures for groundwater monitoring, are commercially available. Procedures are highly reliable and easily maintained (U.S. Environmental Protection Agency and U.S. Air Force Environics Directorate 1993).

Limitations on the use of monitored natural attenuation include the following (U.S. Environmental Protection Agency and U.S. Air Force Environics Directorate 1993):

- a.* Extended time period to achieve cleanup goals.
- b.* Difficulty in obtaining regulatory and community acceptance.
- c.* Difficulty of demonstrating attenuation mechanisms.

For explosives the following technical limitations are imposed by the current state of the science.



- a. Possibly the most important attenuation mechanism for TNT is immobilization by interactions between TNT transformation products and soil components. However, monitoring immobilization processes is restricted to measuring reductions in mass of TNT and its transformation products in groundwater over time. Removal and analysis of the complex, insoluble products of immobilization are not technically feasible at this time. Therefore, the current state of the science does not provide methods for following in situ immobilization processes by direct biological or geochemical measurements. Tests conducted on site material can define the site potential for immobilization (see Chapter 3).
- b. Since microbial mineralization is primarily co-metabolic, degradation rates in natural systems are typically so slow that products (e.g., nitrates, ammonia, methane, and carbon dioxide) do not accumulate in sufficient quantities to be distinguished from background levels. Sites in which groundwater is atypically high in organic carbon, e.g., sites receiving leachate from a feedlot or other high carbon wastes, may accumulate measurable degradation products of the explosives.
- c. Biomarker techniques, including laboratory radioassays and lipid and nucleic acid analyses using site material, measure degradation *potential* in the aquifer, but do not demonstrate in situ degradation. These tests are not currently widely conducted, and they contribute to the weight-of-evidence only.

Immobilization of TNT is best demonstrated by reduction in contaminant mass (mass of parent compounds and transformation products) over time, which can be determined through a carefully executed groundwater-monitoring plan. Site capacity for attenuation of explosives by all operative processes, i.e., adsorption, immobilization, and degradation, can be measured in the laboratory using aquifer material and groundwater from the site in batch partitioning tests. Potential for biodegradation can be determined in the laboratory with radioassays using site material.

## Remedial Alternative Selection Process

The DoD typically responds to the uncontrolled release of hazardous substances under the requirements of either the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, or Superfund) or the Resource Conservation and Recovery Act (RCRA). Although the terminology used under each authority is different, the basic process is similar. In each case the identification and selection of the appropriate response to the release of hazardous substances are conducted in an orderly, phased approach. The similarities and differences of the response action processes under the statutes are illustrated in Figure 4. To simplify this presentation, the following discussion focuses on the CERCLA process and uses CERCLA terminology.

Where appropriate, the reader should use Figure 4 and Table 1 to crosswalk between the CERCLA and RCRA response action processes.

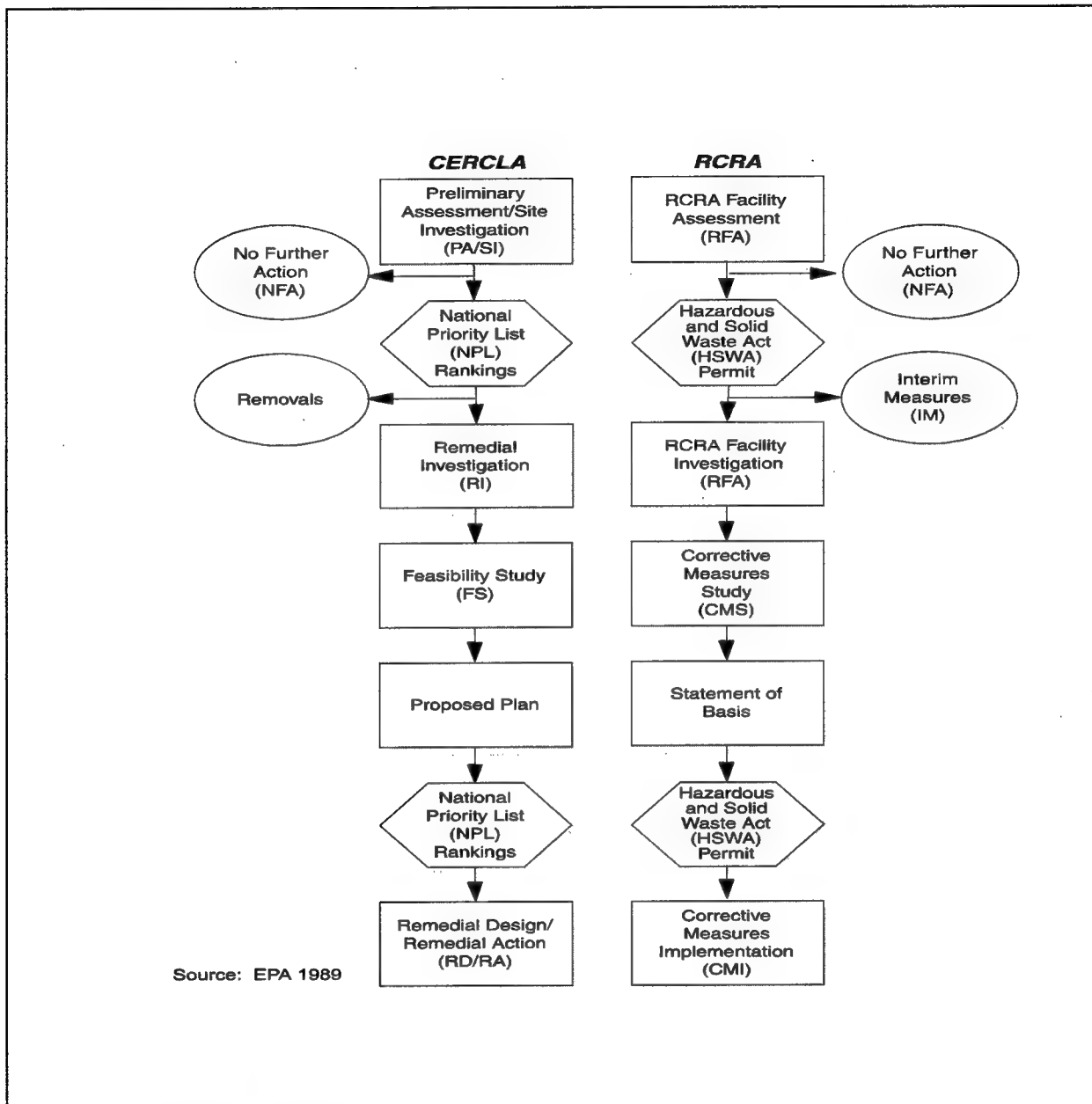


Figure 4. Comparison of CERCLA/RCRA action processes

Under CERCLA, the identification and selection of the appropriate response to the uncontrolled release of hazardous substances are conducted using three steps (Figure 5):

<b>Table 1 CERCLA/RCRA Terminology</b>		
<b>CERCLA Process</b>	<b>RCRA Process</b>	<b>Objective</b>
Preliminary Assessment (PA)	RCRA Facility Assessment (RFA)	Determine the potential for a present or past release—based primarily on historical records
Site Investigation (SI)	No direct equivalent (the RFA may have many of the field investigation aspects of the SI)	Provide sufficient information to determine the need for a full remedial investigation—based on preliminary site data and field sampling for contamination
Remedial Investigation (RI)	RCRA Facility Investigation (RFI)	Characterize the nature, extent, direction, rate, movement, and concentration of releases
Feasibility Study (FS)	Corrective Measures Study (CMS)	Evaluate potential remedial actions and provide sufficient information to decision makers to allow an informed decision to be made

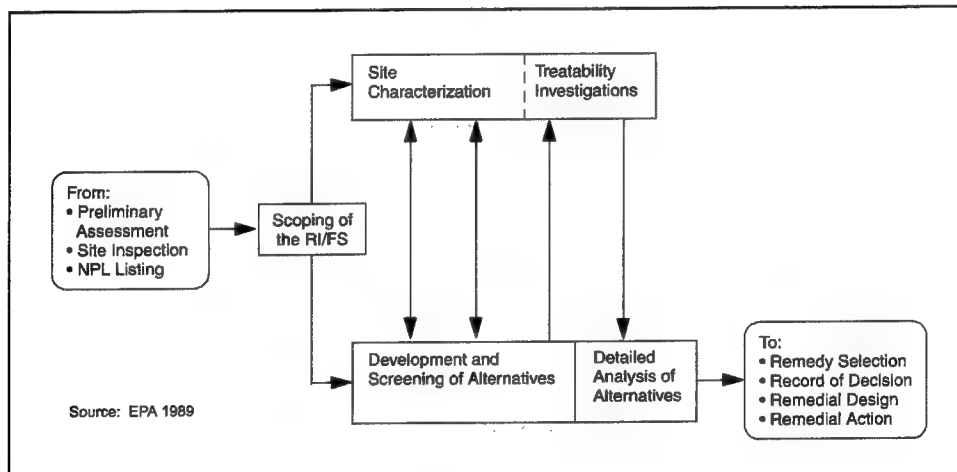


Figure 5. Remedial action evaluation process

- a. Preliminary assessment (PA).
- b. Site investigation (SI).
- c. Remedial investigation/feasibility study (RI/FS).

Alternative selection may be viewed as a series of analytical steps that require making successively more specific definitions and evaluations of potential remedial activities. The alternative development, screening, and detailed evaluation process follow the general guidelines presented in *Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA–Interim Final* (U.S. Environmental Protection Agency (EPA) 1989).

The alternative development and screening process is illustrated in Figure 6. Alternatives passing the screening process are subjected to a detailed evaluation process incorporating nine criteria, as shown in Figure 7. The interrelationship of the alternative screening and detailed evaluation process is illustrated in Figure 8.

Currently, monitored natural attenuation is considered as a potential remedial alternative in both Superfund and RCRA programs. Formal and informal guidance documents the viability of the process and describes how it may be evaluated as a remedial alternative. Brief descriptions of the applicable policy and guidance are provided below.

In general, both State and Federal regulators make the decision whether to accept or reject monitored natural attenuation as a remedial alternative based heavily on site-specific factors such as contamination type, contamination concentration, and distance to potential receptors.

### **Federal policy and guidance**

**Superfund regulations.** Within the regulatory framework of Superfund, the preamble to the NCP contains a discussion of the appropriateness of monitored natural attenuation for the cleanup of groundwater (*Federal Register* 1990a). The EPA acknowledges that monitored natural attenuation may be a viable alternative under certain conditions. EPA stresses that the use of monitored natural attenuation does not imply that the groundwater will not be cleaned up, but that various mechanisms will reduce contaminants to concentrations that are protective of human health and the environment in a "timeframe comparable to that which could be achieved through active restoration."

The rationale behind the conditional support of monitored natural attenuation as a remedial alternative is based upon several site-specific factors. For example, although groundwater extraction and treatment methods can be effective for reducing concentrations of highly contaminated groundwater, such methods are often less effective in further reducing low levels of contamination necessary to achieve remedial goals (Keeley 1989). In response, EPA states that such systems may be periodically evaluated and, when appropriate, monitored natural attenuation may be used to complete the cleanup (*Federal Register* 1990a; Keeley 1989; EPA 1993).

The time required to achieve remedial goals is an issue that may affect the viability of monitored natural attenuation. Current EPA policy is that remediation time frames must be reasonable given specific site conditions. Rapid restoration of groundwater is favored where groundwater is currently (or likely to be in the near future) the source of a drinking water supply or where groundwater feeds into, or is connected to, sensitive or vulnerable aquatic ecosystems. In contrast, factors such as location, proximity to population, and likelihood of exposure may allow for the extended time frames that are more commonly associated with monitored natural attenuation.

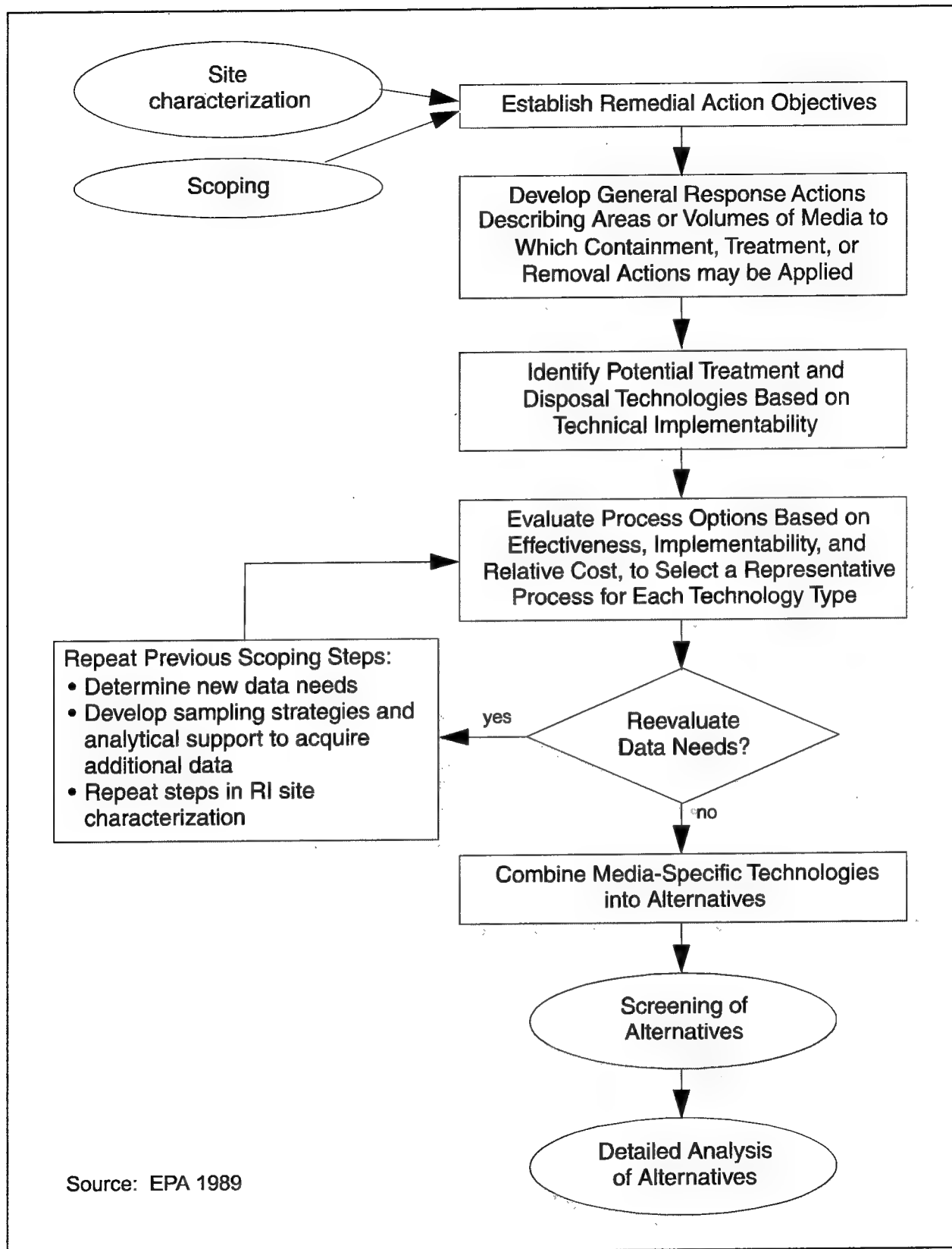


Figure 6. Alternative development and screening

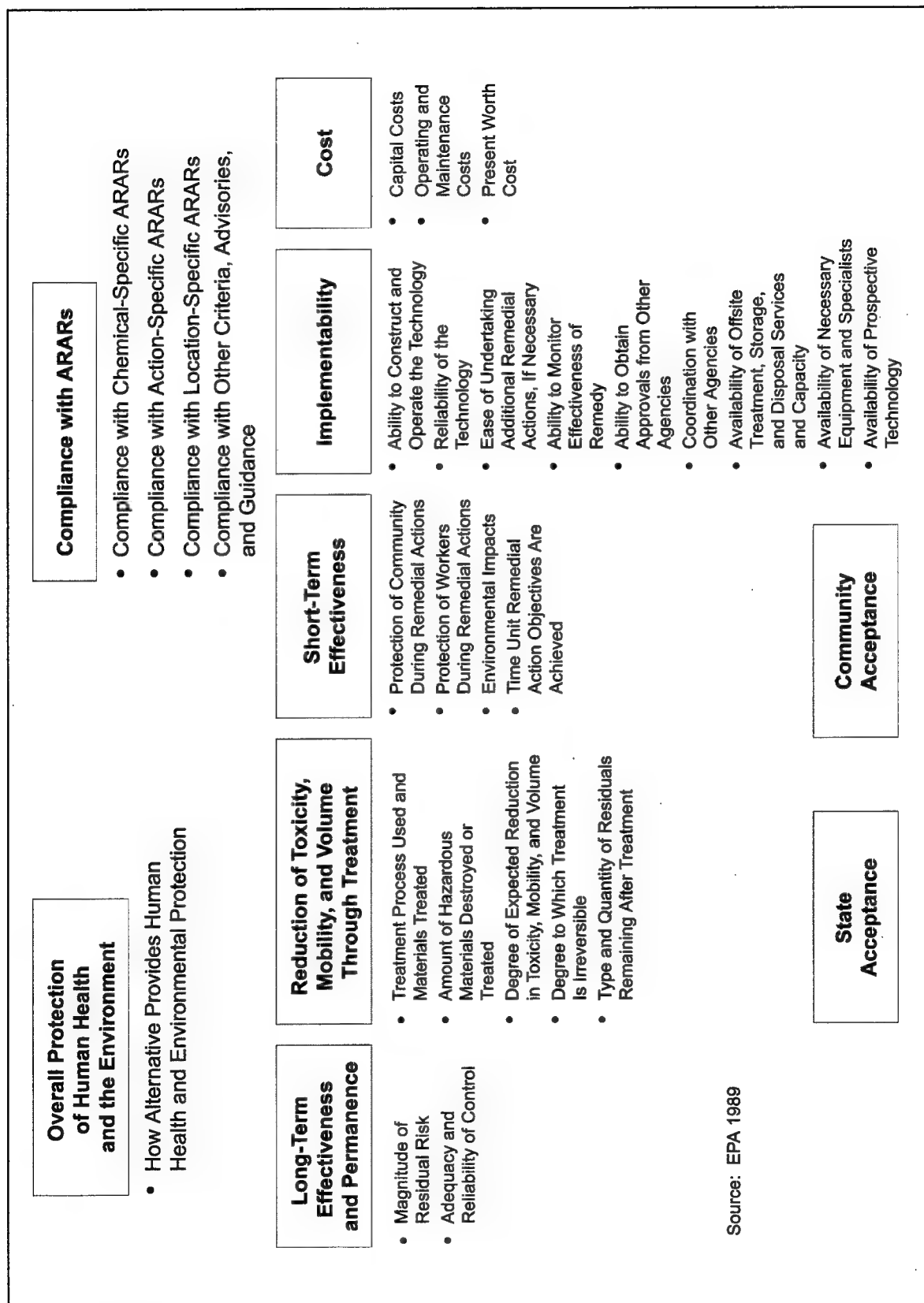


Figure 7. Detailed analysis of alternatives

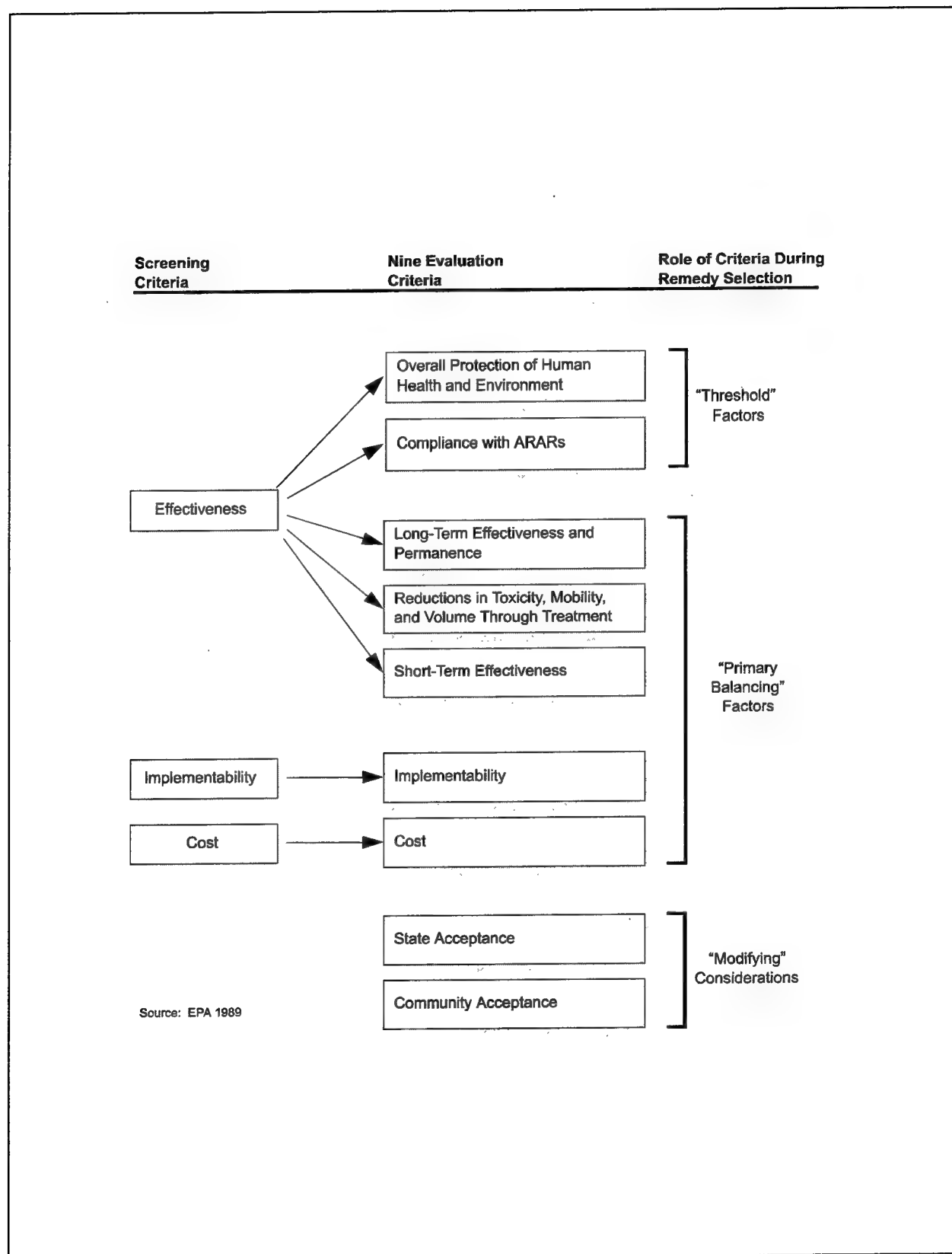


Figure 8. Relationship between screening criteria and detailed evaluation

**RCRA Corrective Action regulations.** Monitored natural attenuation is addressed in EPA policy regarding RCRA Corrective Actions as presented in the preamble to the proposed Subpart S rule (*Federal Register* 1990b). In this context, the policy is similar to that described in the preamble to the NCP. Specifically, monitored natural attenuation may be considered as a remedial alternative in situations where cleanup standards can be achieved in a reasonable time frame and the likelihood of exposure is minimal.

Monitored natural attenuation is also specifically addressed with respect to the evaluation of alternative technologies for the cleanup of underground storage tank sites regulated under RCRA (EPA 1994a). This guidance specifically addresses petroleum hydrocarbon contamination; however, many of the criteria used to evaluate monitored natural attenuation (and seven other alternatives) and other decision-making aspects have application to other contamination. The document describes steps to be taken to evaluate alternative technologies as well as various contaminant and site characteristics that will have an impact on the effectiveness of monitored natural attenuation.

**EPA Natural Attenuation Policy.** In April 1999, EPA's Office of Solid Waste and Emergency Response (OSWER) issued a Directive (OSWER Directive Number 9200.4-17) entitled *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites* (EPA 1999). This directive provides a summary of EPA policy regarding the use of monitored natural attenuation for the remediation of contaminated soil and groundwater at sites regulated under all programs administered by EPA's OSWER, including Superfund, RCRA Corrective Action, and Underground Storage Tanks.<sup>1</sup> The policy provides clarification of some important issues regarding the evaluation and implementation of monitored natural attenuation. These issues include the following:

- a. EPA does not generally view natural attenuation as a "no action" remedy. For this reason, the term "monitored natural attenuation" is preferred.
- b. Consideration of monitored natural attenuation does not reflect a deviation from existing regulations and policies that address remedy selection.
- c. Monitored natural attenuation is not to be considered a default or presumptive remedy at any site. Although provisions are made for the determination of technical impracticality at Superfund and RCRA sites, these determinations are to be used to justify a change in remediation objectives based on the unavailability of capable and responsive

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<sup>1</sup> The document is available for downloading from the World Wide Web at <http://www.epa.gov/swerust1/directiv/d9200417.htm>. Paper copies may be ordered from National Technical Information Service (NTIS). The EPA document number is EPA-540-R-99-009, and the NTIS document number is PB99963315. The phone number for NTIS is (703)487-4650. (For rush service, call 1-800-NTIS.) NOTE: NTIS charges a fee for copies of documents and other materials. The document was published in the *Federal Register* at 64 FR 25039-25040 Monday, May 10, 1999 (FRO51099.PDF, Adobe PF format, 6KBytes).



technologies. In such cases, the ultimate cleanup strategy must still be protective of human health and the environment. This alternative strategy may or may not employ monitored natural attenuation as a remedy or part of a remedy.

As part of the EPA clarification, monitored natural attenuation is identified as a potential means of providing a remedy for subsurface contamination and may be evaluated and compared with other viable remediation methods. A summary of the general elements and related factors, issues, and actions to be addressed or considered in the evaluation of monitored natural attenuation is provided in Table 2.

EPA recommended that source control actions be given the highest priority at sites under consideration for a monitored natural attenuation remedy. Such actions can enhance the effectiveness of monitored natural attenuation by reducing the amount of time required to reach remediation goals and by eliminating the potential for continued releases that can affect the course of monitored natural attenuation and pose risks to potential receptors.

EPA provides the following guidance concerning the determination of a “reasonable” timeframe for achieving remediation objectives:

- “-A reasonable timeframe is one that is comparable to that which could be achieved through active remediation
- The most appropriate timeframe must be determined through analysis of all appropriate remedy alternatives
- For restoration of groundwater to beneficial uses, a comparison of restoration alternatives from most aggressive to passive is necessary to establish range of time required to achieve remediation objectives
- A measured decrease in contaminant concentrations of **at least one order of magnitude** is necessary to determine appropriate rate law to describe rate of attenuation, and to demonstrate that the estimated rate is statistically different from zero at a **95 % level of confidence.**”

**Army policy.** At the present time, the Army has an interim policy related to the use of natural attenuation as an appropriate remedial action ([www.usace.army.mil/inet/usace-docs/review/cemp-002.pdf](http://www.usace.army.mil/inet/usace-docs/review/cemp-002.pdf)) (Appendix F). This policy is consistent with EPA policy and requires that natural attenuation be considered along with engineered remediation alternatives. In fact, an engineered remedial alternative will not be approved unless data exist to prove that natural attenuation is inappropriate for a site cleanup. The issues of prioritization and sequencing of work, timeliness of cleanup, ease of technology implementation, and affordability of treatment must be assessed for each site. A greater participation among the regulatory, public, and industrial communities is a DoD goal.

**Table 2****Summary of EPA Policy for the Evaluation of Monitored Natural Attenuation as a Remedial Alternative**

<b>General Elements in the Evaluation of Monitored Natural Attenuation</b>	<b>Related Factors, Issues, and Actions</b>
Role of monitored natural attenuation in the remedy selection process	<ul style="list-style-type: none"> <li>• May be an appropriate alternative under a limited set of circumstances</li> <li>• May be evaluated and compared with other viable remedies during the study phases leading to the selection of remedy</li> <li>• May be cautiously evaluated as a sole remedy</li> <li>• May be evaluated as a component of a total remedy that includes engineered remedial measures</li> <li>• May be evaluated as a follow-on to engineered remediation</li> <li>• Must not be considered a default or presumptive remedy</li> </ul>
General requirements for the selection of monitored natural attenuation as a remedy	<ul style="list-style-type: none"> <li>• Must meet all relevant remedy selection criteria</li> <li>• Must be fully protective of human health and the environment</li> <li>• Must meet site remediation objectives within a reasonable time frame compared with other methods</li> <li>• Must be supported by detailed site-specific information that demonstrates its efficacy</li> <li>• Must evaluate all contaminants that represent an actual or potential threat to human health or the environment</li> <li>• Must include opportunities for public involvement to both educate and gather feedback from interested parties</li> </ul>
Requirements for the demonstration of the effectiveness of monitored natural attenuation through site characterization	<ul style="list-style-type: none"> <li>• Site characterization will involve the collection and development of data and conduct of analyses to demonstrate that natural attenuation can meet the remedial action objectives. At a minimum, the following actions will be required: <ul style="list-style-type: none"> <li>– Collect data to define nature and distribution of contamination sources</li> <li>– Collect data and conduct analyses to define the extent of the groundwater plume and potential impacts on receptors</li> </ul> </li> <li>• Other data and information required will be dependent upon site-specific characteristics, the nature of the contaminants, and the natural attenuation process(es) being evaluated</li> <li>• Data quality must be adequate, levels of confidence on attenuation rates documented, and sensitivity analyses performed to determine dependence of calculated remediation timeframes on uncertainties in rate constants and other factors</li> </ul>
Requirements for the evaluation of the efficacy of monitored natural attenuation through site-specific lines of evidence	<ul style="list-style-type: none"> <li>• The evaluation of efficacy may include the collection and evaluation of the following data and information: <ul style="list-style-type: none"> <li>– Historical groundwater and soil data that clearly demonstrate declining contaminant concentrations and/or masses</li> <li>– Hydrogeologic or geochemical data that can indirectly demonstrate the mechanisms involved in natural attenuation at the site and the rate at which contaminant reductions occur</li> <li>– Data from field or microcosm studies that demonstrate the occurrence of a natural attenuation process and its ability to effect contaminant reductions (particularly through degradation)</li> </ul> </li> </ul>
Requirements for the implementation of monitored natural attenuation	<ul style="list-style-type: none"> <li>• Source control and performance monitoring should be fundamental components of the remedy</li> <li>• Institutional controls may be necessary</li> <li>• Performance monitoring should continue as long as contamination remains above cleanup levels</li> <li>• Remedies employing natural attenuation should include evaluation of need for one or more contingency remedies</li> </ul>

(Adapted from EPA 1999)

## State policy and guidance

As more knowledge and experience are gained regarding monitored natural attenuation (particularly in the area of contamination of groundwater by petroleum hydrocarbons), interest is increasing among the States in developing guidance and policy for the evaluation and implementation of natural attenuation as a remedy. The results of 1996 survey of more than 125 environmental regulators from all 50 States' agencies indicated a tendency toward the acceptance of monitored natural attenuation as a remedial alternative (Ritz 1996a). Two States, North Carolina and New Jersey, have prepared stand-alone documents that describe how and when monitored natural attenuation may be used (Spiese 1996). In general, these documents specify certain requirements for the implementation of monitored natural attenuation, including source removal, receptor analyses, modeling to predict plume degradation, and monitoring.

Despite an apparent increase in interest in monitored natural attenuation, the level of acceptance varies considerably among the States. Results of the 1996 survey were focused on attitudes regarding monitored natural attenuation as a stand-alone remedial option for groundwater contaminated with volatile organic compounds. The results of the interviews reflect four general attitudes or positions among the regulators.

- a. Regulatory agency has no specific guidelines or policies, but would consider monitored natural attenuation on a case-by-case basis.
- b. Regulatory agency has no comprehensive, written policy concerning monitored natural attenuation, but some informal guidelines exist that allow for its use.
- c. Regulatory agency does not explicitly address monitored natural attenuation in its policies; however, monitored natural attenuation mechanisms were considered in the drafting of these policies.
- d. Regulatory agency has developed written guidelines specifically addressing the evaluation and/or use of monitored natural attenuation.

A summary of the findings of these interviews is presented in Table 3. This table is presented primarily to provide an indication of the various attitudes concerning monitored natural attenuation. The table should be reviewed in the following context:

- a. Survey reflects responses directed toward contamination of groundwater by volatile organic compounds. They may or may not be applicable to other contaminants or environmental media.
- b. Regulatory attitudes and policies/guidelines regarding monitored natural attenuation as a remedy are evolving. At the time of the 1996 survey, at least 41 States indicated that policies/guidelines affecting monitored

**Table 3**  
**Summary of Findings of State Regulatory Agency Interviews Regarding**  
**Monitored Natural Attenuation**

Category	State or State Agency/Group	
<b>No Policies/Guidelines But Would Consider</b>	Alabama (Hydrogeology Unit) Alaska Arizona (Soil and Groundwater Standards Development) Arkansas (Hazardous Waste Section/Water Division) California (Water Resources Control Board) Colorado (non-UST) Delaware (Groundwater Protection Program/RCRA Program) Florida (Hazardous Waste) Georgia (Hazardous Waste) Idaho (CERCLA/RCRA) Indiana Iowa (Uncontrolled Sites) Kansas Kentucky (non-UST) Louisiana Maine (Bureau of Hazardous Material & Solid Waste) Maryland (Oil Control Program/ Superfund) Minnesota (Superfund)	Mississippi Missouri (non-UST) Montana (non-UST) Nebraska Nevada New Mexico (RCRA Section/UST Section) New York Ohio (Superfund) Oregon (Cleanup Policy and Program Development Section) Pennsylvania (CERCLA/Hazardous Waste/Solid Waste) Rhode Island South Dakota (RCRA) Tennessee Texas Utah (non-UST) Virginia Washington West Virginia Wyoming (non-UST)
<b>Informal Policies/Guidelines</b>	Alabama (UST Corrective Action) Arizona (UST Section) Arkansas (Regulated Storage Tank Division) California (Department of Toxic Substance Control) Delaware (UST Section)	Maryland (Hazardous Waste Program) Missouri (LUST Unit) Montana (UST Section) North Dakota Ohio (Voluntary Action Program) Wyoming (UST Section)
<b>Natural Attenuation Implicit in Policies/Guidelines</b>	Colorado (Oil Inspection Section) Connecticut Delaware (Site Investigation and Restoration Branch) Florida (Dry Cleaning Solvent Cleanup Program/Engineering and Technical Support) Georgia (UST Management Program) Hawaii Illinois Iowa (UST Section) Maine (UST Section)	Massachusetts Michigan (UST Section) New Hampshire New Mexico (Remediation Program) Ohio (BUSTR Program) Oklahoma Oregon (UST Section) Pennsylvania (Environmental Cleanup Program) South Carolina (non-UST) South Dakota (UST Section) Utah (UST Section) Vermont
<b>Written Policies/Guidelines</b>	Idaho (Remediation Bureau) Kentucky (UST Section) Michigan (Environmental Response Division)	Minnesota (Tanks and Spills Section) New Jersey North Carolina South Carolina (UST Section) Wisconsin
Source: Ritz 1996a,b		

natural attenuation were under review and may be subject to change (Ritz 1996b).

- c. Significant differences in attitudes and policies/guidelines between the various environmental agencies within a single State are likely.
- d. Willingness to consider monitored natural attenuation as a remedy for groundwater contaminated with volatile organic compounds is widespread.
- e. Consulting the appropriate regulatory agency regarding policies/guidelines for the evaluation and implementation of monitored natural attenuation as a remedy on a site-by-site basis is critical.

### **Monitored natural attenuation of nonexplosives contaminants**

Over the past few years, the development of guidance documents or protocols for the evaluation and/or implementation of monitored natural attenuation for specific contaminated media has been initiated. Of these initiatives, three have resulted in the publication of guidance documents or protocols. The first, *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater*,<sup>1</sup> was sponsored by the Air Force Center for Environmental Excellence (AFCEE) with technical contributions provided by representatives of AFCEE and EPA's Robert S. Kerr Laboratory (Wiedemeier et al. 1997).<sup>1</sup> This document provides a formal protocol for the collection and analysis of data necessary to accomplish an evaluation of the fate of fuel hydrocarbons in groundwater. The results of the evaluation may then be used to support the consideration of monitored natural attenuation (or "intrinsic remediation") with long-term monitoring for restoration of groundwater contaminated with fuel hydrocarbons.

The scope of activities addressed by the AFCEE protocol includes those in the flowchart presented in Figure 9. This flowchart provides an illustration of the information to be developed in the consideration of monitored natural attenuation and the key regulatory decision points in the implementation of the option. Each of the activities illustrated in the protocol is described in detail in the document.

The second document supporting the consideration of a monitored natural attenuation remedial option is the *Guidance Handbook on Natural Attenuation of Chlorinated Solvents*.<sup>2</sup> This handbook was prepared in 1996 by the Bioremediation of Chlorinated Solvents Consortium of the Remediation

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<sup>1</sup> This protocol is available from the AFCEE Technology Transfer Division, Brooks Air Force Base, San Antonio, TX.

<sup>2</sup> This handbook is available for downloading from the World Wide Web <http://www.epa.gov/ada/report.html>.

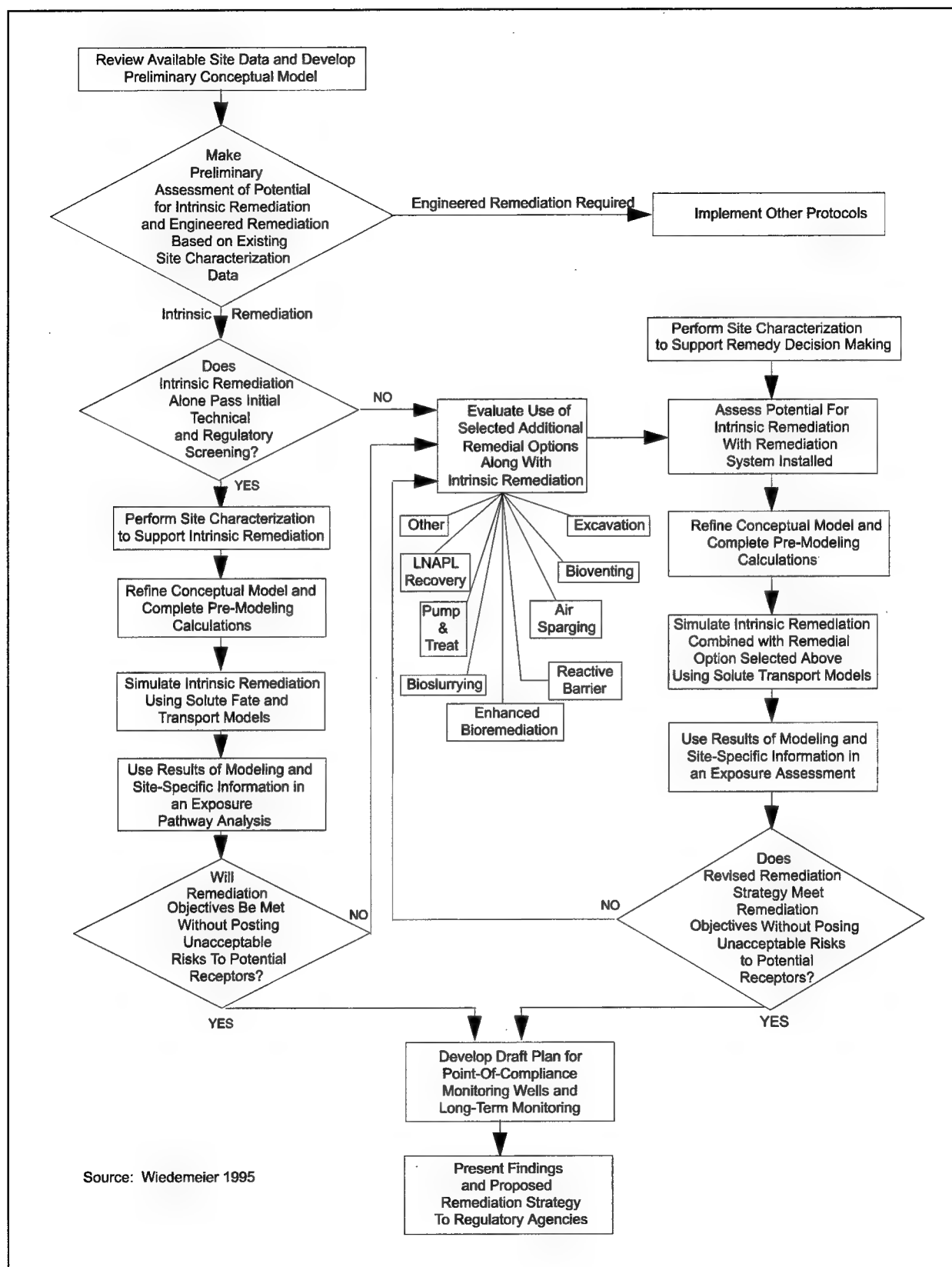


Figure 9. Flowchart for intrinsic remediation of fuel hydrocarbons

Technologies Development Forum (RTDF), a collaboration between the public and private sectors to develop innovative solutions to complex hazardous waste problems. As stated in the foreword, the handbook is a “quick reference book that distills the essence of the current science and practice of natural attenuation of chlorinated solvents.” As such, the document is an informative and easy-to-read description of the potential for monitored natural attenuation, the technical aspects of monitored natural attenuation, methods for evaluating monitored natural attenuation, and a step-wise process to evaluate and implement monitored natural attenuation at sites contaminated with chlorinated solvents. This step-wise process for evaluation and implementation is summarized in the flowchart presented in Figure 10.

The third is the AFCEE protocol for chlorinated solvents entitled “*Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater*”<sup>1</sup> (EPA 1998).

## Applications of Natural Attenuation

To provide an indication of the willingness of site managers and regulators to consider natural attenuation, a few examples of where natural attenuation has been documented, implemented, or proposed for implementation are provided below. Of particular interest to readers and users of this report is the summary of the selection of natural attenuation at Sierra Army Depot as part of the remedy for groundwater contaminated with explosives and other organics. This example provides not only an indication of the potential of natural attenuation at similar sites, but also illustrates the type of supporting activities that might be required to implement the remedy.

## Summary

The following tables are provided as summaries of considerations that may affect an initial decision to proceed with monitored natural attenuation as a remedy. The first table, Table 4, contrasts some of the primary potential advantages associated with monitored natural attenuation with possible limitations or disadvantages.

A list of site-specific characteristics that may support the successful implementation of monitored natural attenuation is provided in Table 5. This table was developed through a review of regulatory policy and guidance and a review of monitored natural attenuation-based RODs as described earlier in this section.

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<sup>1</sup> This handbook is available for downloading from the world wide web  
[http://www.dep.state.pa.us/dep/deputate/airwaste/wm/remserv/biotreat/Tech\\_Ref.htm](http://www.dep.state.pa.us/dep/deputate/airwaste/wm/remserv/biotreat/Tech_Ref.htm).

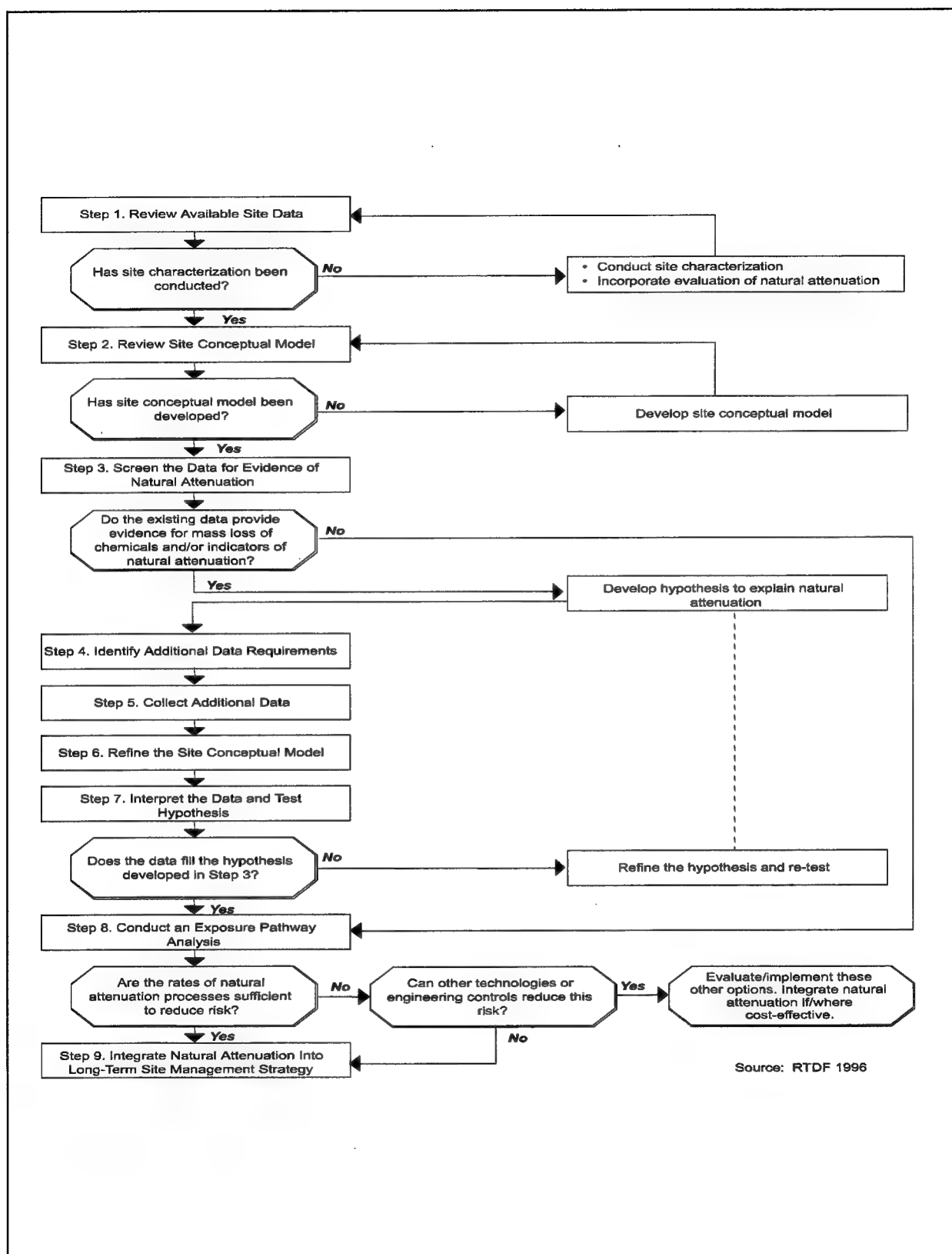


Figure 10. Flowchart to evaluate and implement monitored natural attenuation at sites contaminated with chlorinated solvents



<b>Table 4 Potential Advantages and Disadvantages of Monitored Natural Attenuation Remedial Alternative</b>	
<b>Advantages</b>	
Lower cost	Costs are likely to be less than for engineered remedies.
Minimal exposures to hazardous materials	Monitored natural attenuation is conducted with minimal disruption of contaminated media, thus reducing the potential for worker exposures because of the handling and transport of materials and wastes
Nonintrusive	Monitored natural attenuation may be desirable where contamination exists at an active facility and minimal disruption of ongoing activities is required Monitored natural attenuation may be desirable where engineered remedial measures are not practical or possible because of inaccessible contamination (e.g., underneath a building)
Easily implemented	Some factors affecting the implementation of engineered remedial alternatives (e.g., construction and operation of remediation system, equipment availability and reliability, and availability of services) may be simplified through the use of monitored natural attenuation, thus reducing the time and costs for implementation
<b>Disadvantages</b>	
Long time frame	Very long time frames may be required to meet cleanup goals
Long-term monitoring	Long-term monitoring will be required to ensure protection of potential receptors
A "new" technology	Documented site experience with monitored natural attenuation is generally limited to readily biodegradable contaminants -- experience with explosives is currently limited

<b>Table 5 Factors Favoring Selection of Monitored Natural Attenuation as a Remedial Alternative</b>	
<b>Category</b>	<b>Characteristics</b>
Characteristics of contamination	Limited areal extent of contamination Very old source of contamination Contaminant concentrations have decreased over time Contamination source confined to unsaturated soil Source has been controlled or removed Low concentrations of contaminants in groundwater reduce the technical and economic feasibility of engineered remedial approaches Well-defined contamination characteristics (e.g., nature and distribution of contaminants) All contaminants are easily biodegraded Mechanisms of attenuation are known and understood and have been demonstrated
Characteristics of site	Significant distance to the nearest human or ecological receptor Limited or no access to contaminated media (e.g., under a building) No nearby bodies of surface water Groundwater is unsuitable for human consumption because of naturally occurring conditions other than contamination No potential for groundwater to affect drinking water sources or environmentally significant groundwater Well-defined and complete hydrogeological and geochemical characterization of groundwater Contaminated groundwater plume is well delineated and is stable in size
Future uses of site	Groundwater is unlikely to be used in the foreseeable future Time to achieve remedial goals will not affect planned future use of the site or affected groundwater
Characteristics of remedy	Monitored natural attenuation to be used in conjunction with engineered remediation measures Monitored natural attenuation to be implemented to provide a follow-on to engineered remediation measures that have already been implemented Remedy will include institutional controls to limit future use and/or implement deed restrictions Remedy will provide for long-term monitoring

# **3 Protocol for Evaluation, Selection, and Implementation of Monitored Natural Attenuation as a Remedial Alternative**

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## **Scope of the Protocol**

The primary requirement for any remedial alternative is that it be adequately protective of human health and the environment. The goal of this protocol is to guide the user to develop, assess, and document site-specific data and information to determine whether monitored natural attenuation can meet this criterion.

Evaluating the feasibility of monitored natural attenuation for explosive-contaminated sites is impacted by several factors that distinguish such sites from those contaminated with petroleum hydrocarbons or chlorinated solvents. Attenuation through immobilization as well as through biodegradation may contribute to achievement of remediation goals.

The U.S. Environmental Protection Agency identifies the following three “tiers of site-specific information, or ‘lines of evidence’” in OSWER directive 9200.4-17 (EPA 1999):

- (1) “Historical groundwater and/or soil chemistry data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points. (In the case of a groundwater plume, decreasing concentrations should not be solely the result of plume migration. In the case of inorganic

contaminants, the primary attenuating mechanism should also be understood.)”

This line of evidence requires the review of available site data to identify any historical trends in contaminant concentration and contaminant distribution at the site and development of a monitoring program to verify continuing declines in contaminant mass. This line of evidence does not restrict the evaluation to the identification of declining contaminant mass due to biodegradation. Rather, the evaluation considers all potential attenuation mechanisms such as immobilization through physical or chemical means.

- (2) “Hydrogeologic and geochemical data that can be used to demonstrate **indirectly** the type(s) of natural attenuation processes active at the site, and the rate at which such processes will reduce contaminant concentrations to required levels. For example, characterization data may be used to quantify the rates of contaminant sorption, dilution, or volatilization, or to demonstrate and quantify the rates of biological degradation processes occurring at the site.”

This line of evidence requires the search for and identification of potential biological, chemical, or physical markers that directly or indirectly indicate that attenuation of contaminants is occurring at the site through one or more mechanisms and that permit determination of an attenuation rate.

- (3) “Data from field or microcosm studies (conducted in or with actual contaminated site media) which **directly** demonstrate the occurrence of a particular natural attenuation process at the site and its ability to degrade the contaminants of concern (typically used to demonstrate biological degradation processes only).”

Several microcosm studies that can be used to demonstrate attenuation of explosives are described in this protocol.

## Regulatory Coordination

The ability to select and implement monitored natural attenuation as all or part of a remedial approach will depend upon regulatory acceptance. For this reason, coordination with the appropriate regulatory agencies will be a critical part of the selection and implementation procedure. Currently, policy and guidance related to monitored natural attenuation as a remedial action is based upon petroleum hydrocarbons and chlorinated solvents. An important part of regulatory coordination will be highlighting the differences between petroleum hydrocarbons and explosives and how these differences affect the applicable rules and regulations. The proponent must demonstrate an understanding of the cleanup objectives and that monitored natural attenuation will be effective. Regulatory acceptance will depend upon the presentation of a “weight of evidence” that monitored natural attenuation will be more effective or at least as

effective as other remedies in meeting remedial goals. In addition to the typical coordination and negotiations involving the identification of applicable or relevant and appropriate requirements (ARARs) and the establishment of remedial action objectives, the ultimate selection of monitored natural attenuation is likely to require the following:

- a.* Sufficient data to adequately describe the contamination, the subsurface environment, and the likely future fate of the contamination.
- b.* Demonstration that monitored natural attenuation will occur at rates sufficient to meet remedial objectives.
- c.* Evidence that monitored natural attenuation will provide adequate protection of human health and the environment over the long term.

As in any process that involves the identification and evaluation of remedial alternatives for a site, regulatory coordination must be initiated early in the process and maintained throughout the evaluation and selection of alternatives. Such coordination serves three primary purposes:

- a.* Ensures that the evaluation is conducted in accordance with Federal, State, and local regulations or guidelines.
- b.* Provides direction and guidance for the development of alternatives and plans for implementation.
- c.* Informs regulators about the potentially unique circumstances of an explosive-contaminated site.

The specific requirements for the evaluation and implementation of monitored natural attenuation will be dependent upon the regulatory policies as well as views and understanding of the regulators who have responsibility for the site. As a first step to meeting the needs of the regulators, available related guidance and policy at Federal, regional, and State levels must be identified and reviewed. A review of selected guidance and policy is presented in Chapter 2 of this report. As interest in the use of monitored natural attenuation grows and as it becomes a more frequently evaluated remedial alternative, guidance and policy will continue to be developed and to evolve. As a result, identification of the most recent policy or guidance available will be necessary.

As a starting point, the evaluator should review EPA policy (EPA 1999). EPA regional points of contact should also be contacted to identify any relevant region-specific guidance.

As described in Chapter 2, an increasing number of States are developing or revising policy and guidance regarding monitored natural attenuation. This policy and guidance should be identified and reviewed. The evaluator should identify points of contact within the State regulatory agencies with experience in

or responsibility for the evaluation and implementation of monitored natural attenuation.

Coordination will be continued throughout the selection and implementation process. Specific coordination actions are addressed in the procedural steps described in the following section.

## **Procedure**

The following procedure consists of a series of steps requiring data collection, model development, and analyses necessary to complete the following: (a) evaluation of monitored natural attenuation as a remedy for explosive-contaminated sites (Steps 1-8, Figure 11), (b) comparison of monitored natural attenuation to other remedial alternatives (Step 9, Figure 11), and (c) con-siderations for implementing monitored natural attenuation (Step 10, Figure 11). Depending on the available data and information and the evidence gathered to document natural attenuation rates, some steps may be repeated or may be eliminated.

### **Evaluation of monitored natural attenuation as a remedial alternative**

An evaluation of monitored natural attenuation should encompass accumulation of a “weight of evidence” that natural processes are proceeding at a rate sufficient to protect potential receptors and achieve cleanup goals in an acceptable time frame. Use of the “lines of evidence” approach is helpful in this regard. The steps recommended below constitute an iterative process of data evaluation, collection, and interpretation to assess the viability of the monitored natural attenuation alternative. These steps would typically constitute the RI/FS processes preceding remedy selection.

### **Comparison of monitored natural attenuation to other remedial alternatives**

This step of the protocol does not differ significantly from comparisons of any remedial alternatives prior to selection of a treatment technology. Many sources for cost and performance comparisons are available. Comparisons of monitored natural attenuation of explosives to remediation using pump-and-treat and in situ bioremediation are presented in Pennington, Zakikhani, and Harrelson (1999). This step would comprise part of the RI/FS process.

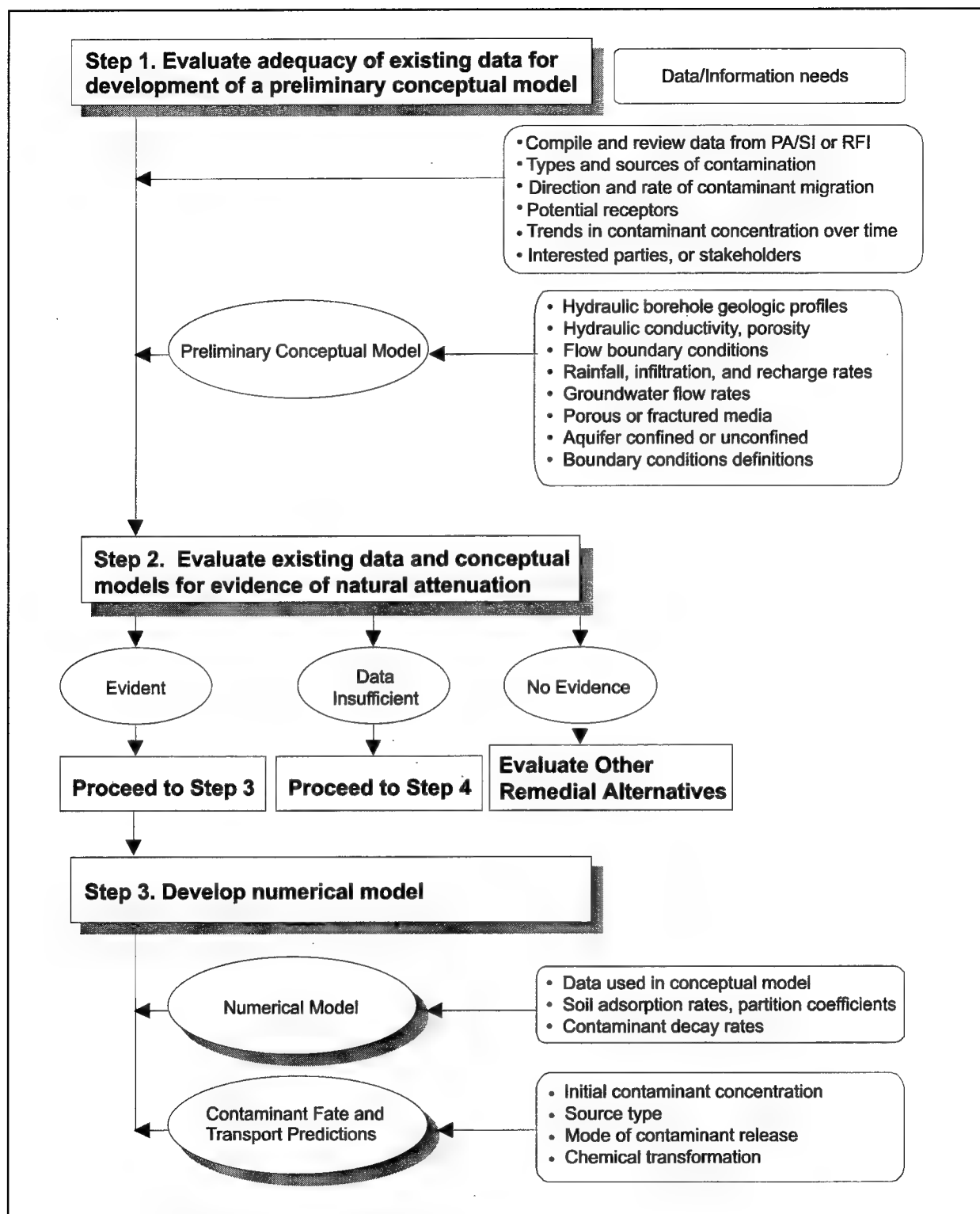


Figure 11. Protocol for monitored natural attenuation of explosives (Sheet 1 of 5)

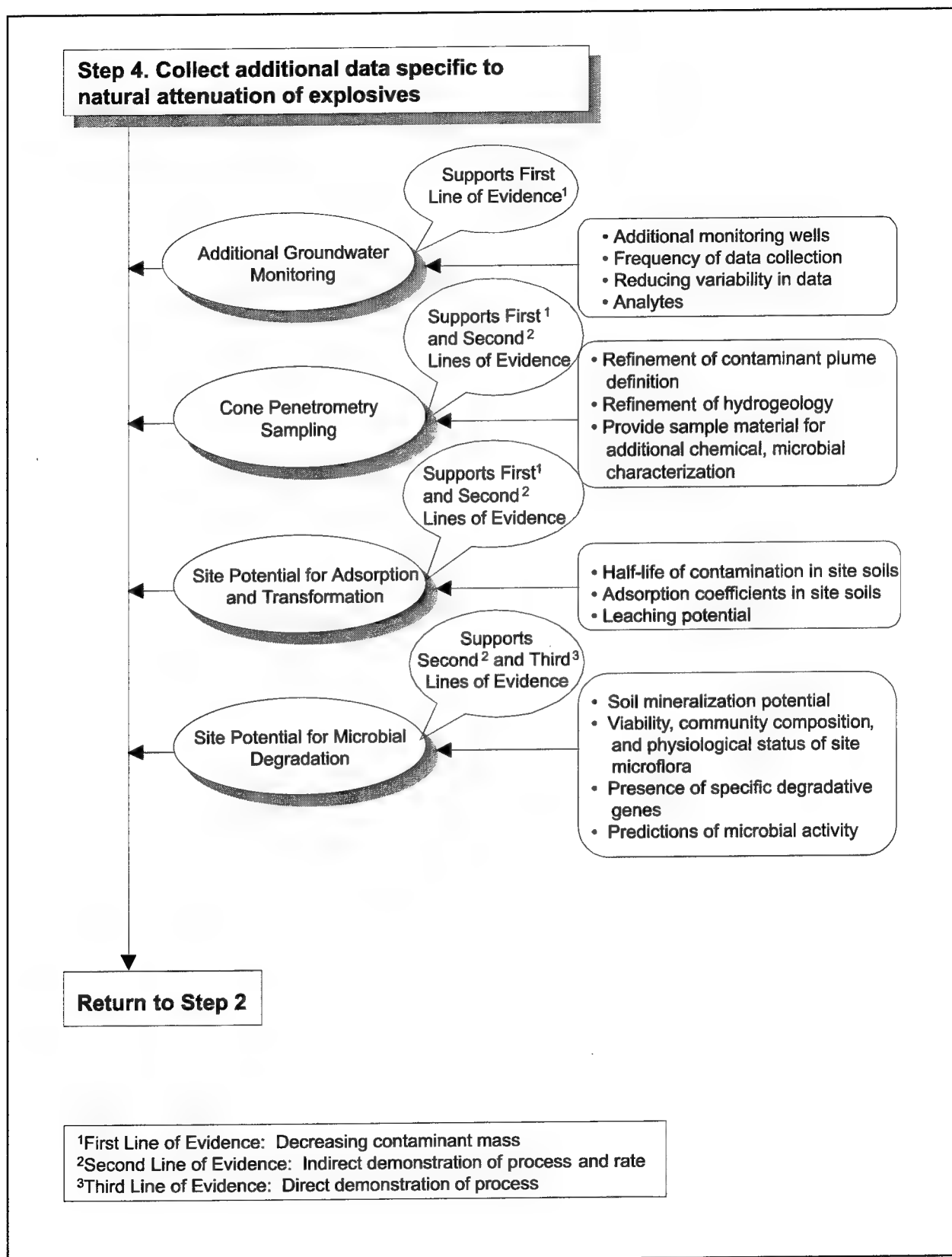


Figure 11. (Sheet 2 of 5)

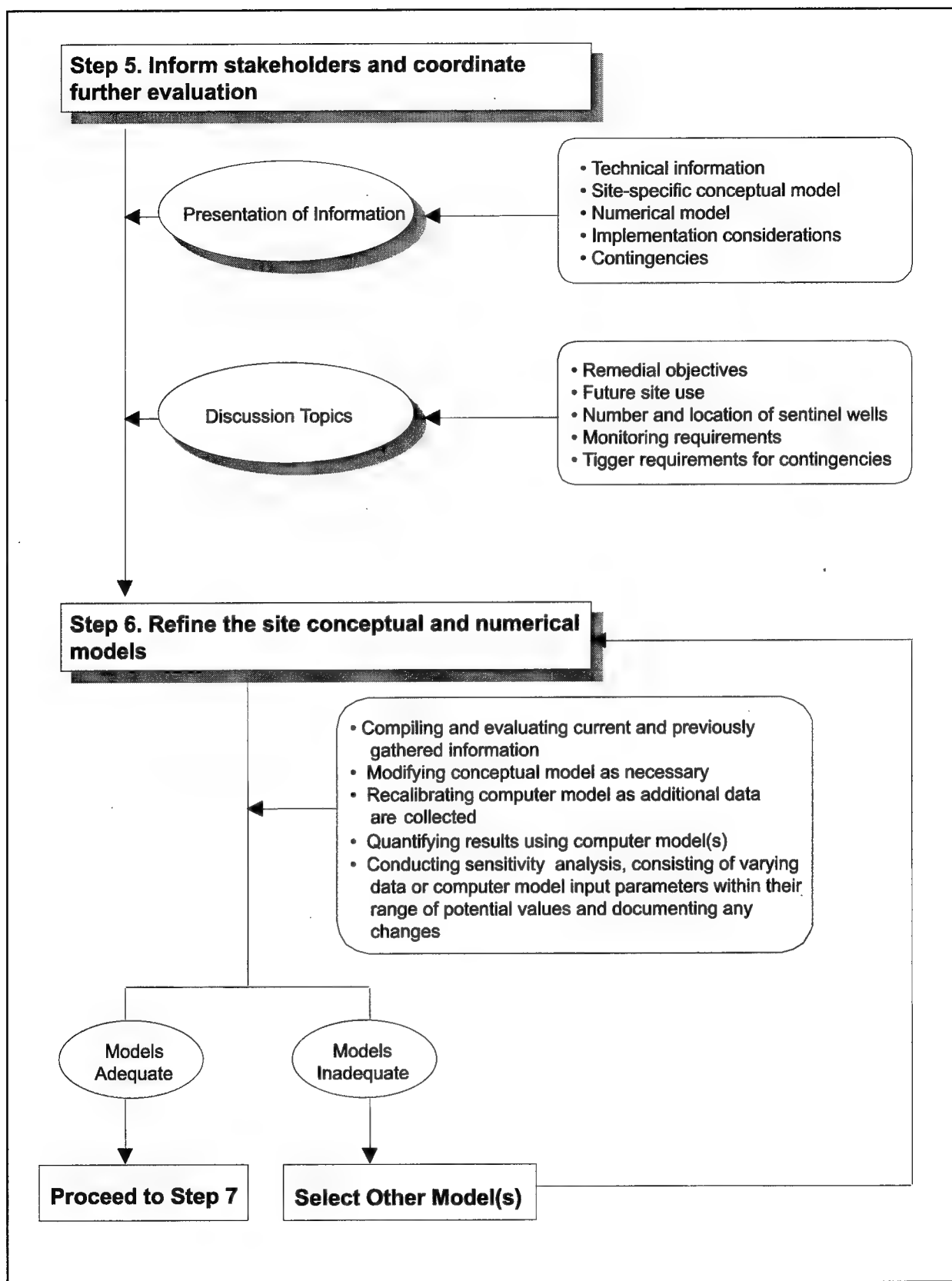


Figure 11. (Sheet 3 of 5)



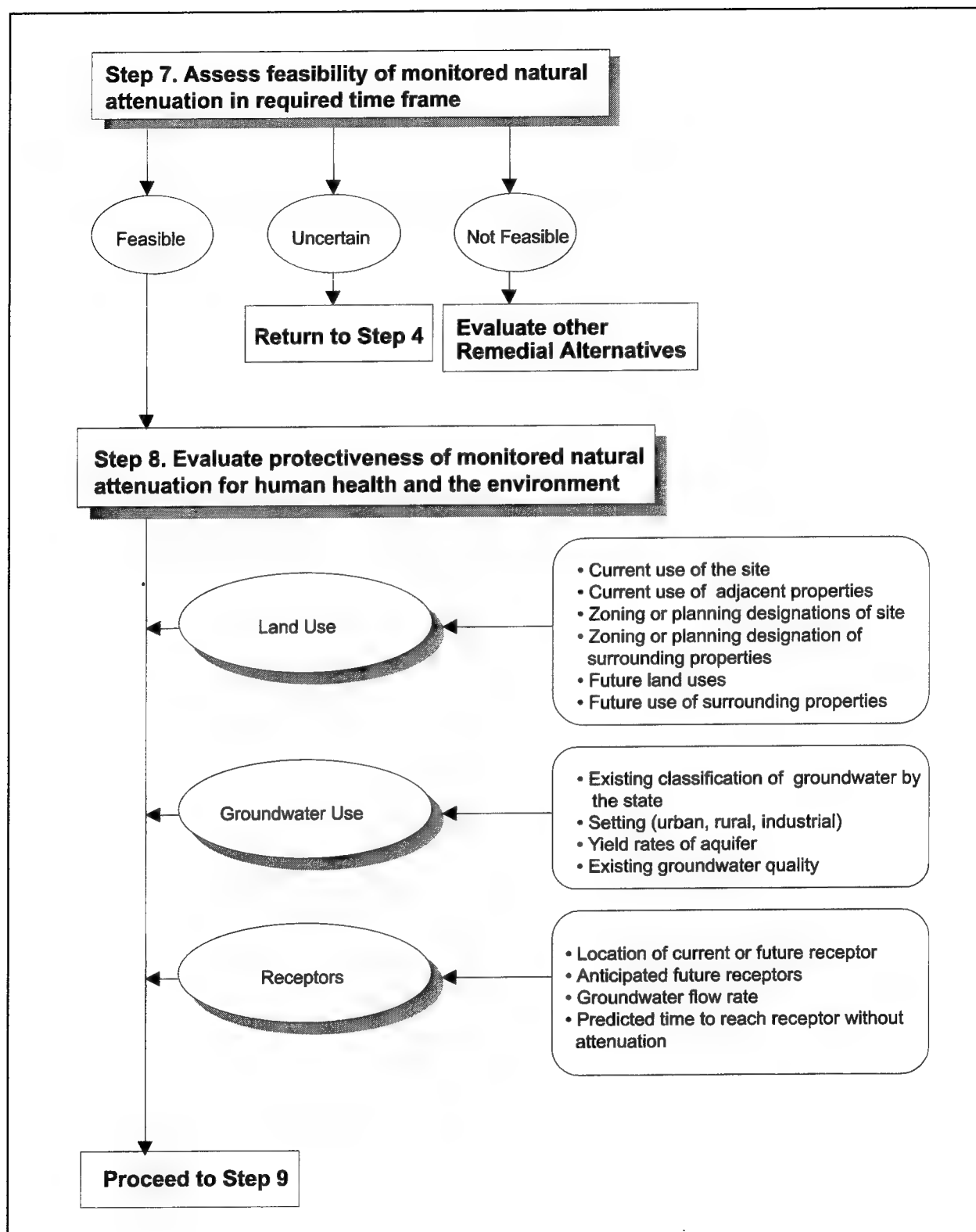


Figure 11. (Sheet 4 of 5)

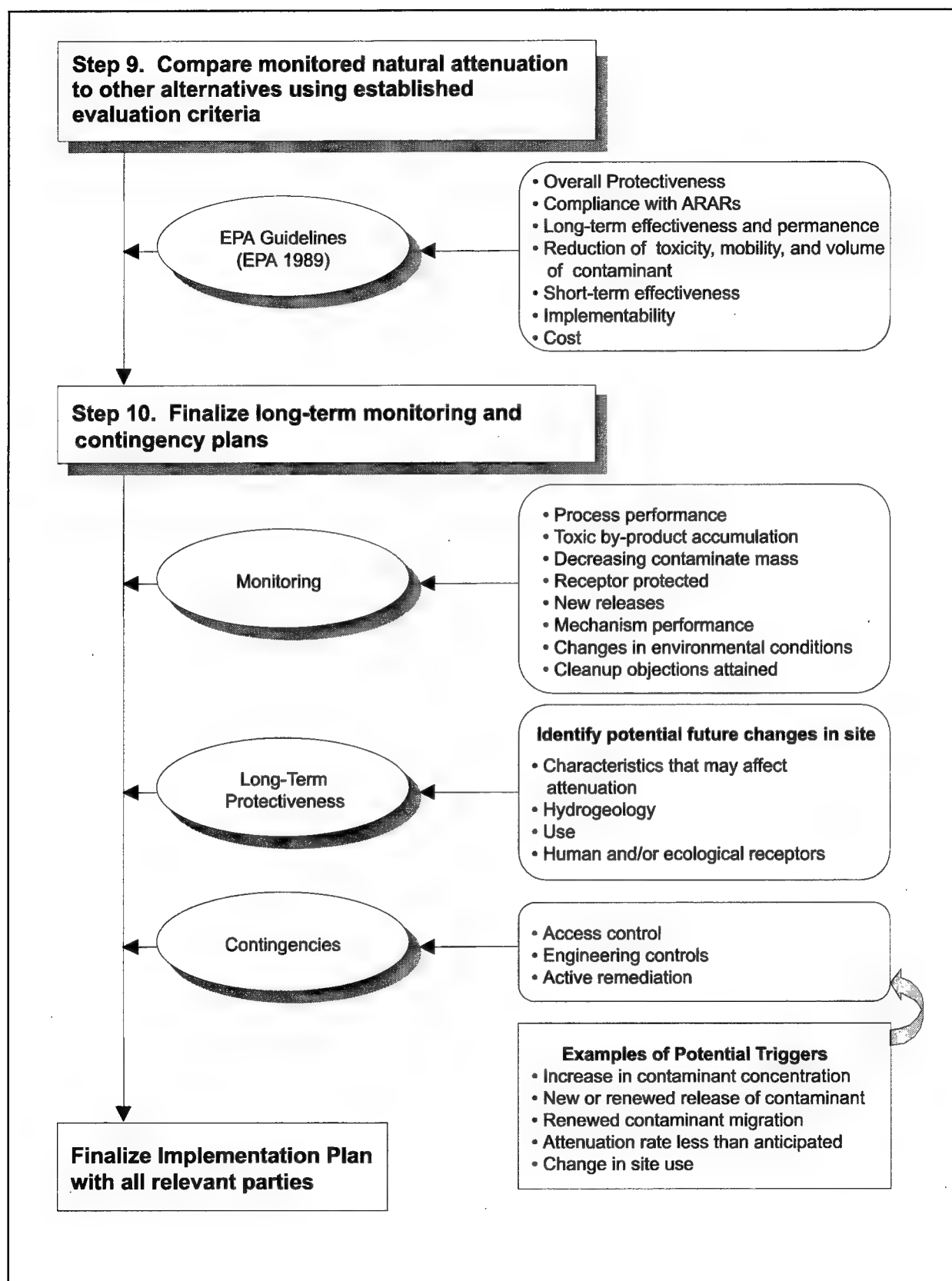


Figure 11. (Sheet 5 of 5)

## Considerations for implementing monitored natural attenuation

An implementation plan must be developed to address issues associated with specific sites. These include development of a long-term monitoring plan and contingency plans should intervention become necessary. This step in the protocol outlines monitoring approaches, considerations for long-term protectiveness, and development of “triggers” for implementation of contingency plans. This step would fall into the RD/RA process.

### Step 1. Evaluate adequacy of existing data for development of a preliminary conceptual model of the site

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*Synopsis: This step requires examination of available data and identification of any gaps in the data that would interfere with development of a preliminary conceptual model of the site. The adequacy of the data for defining the extent of the contaminant plume and the subsurface geology and hydrology will be determined. Historical trends in contaminant concentrations will be sought. Potential receptors will be identified and located.*

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A series of questions relating to general site and contaminant characteristics are presented below. Developing answers to these questions will help in the collection and examination of site-specific data that can be used to develop a preliminary site conceptual model. An illustration of the types of answers that may be generated during this data review is provided in Table 6. An itemized list of specific site characterization data that can be used in developing answers to the following questions is provided in Table 7.

In the initial stage of the evaluation of natural attenuation as a remedy for explosive-contaminated sites, the conceptual model is essentially a hypothetical model. As data are gathered, this hypothesis is modified to represent these new data. The conceptual model is limited by the quality and quantity of the available data.

A conceptual model combines available hydrogeologic, contaminant, potential transport pathway and potential receptor data into a consistent understanding of site transport conditions (Table 8).

Once an initial conceptual model has been developed, it must be verified and supported with quantitative data (Table 9). The data may be obtained from the field or estimated from existing data. In the context of this protocol, the distinction between conceptual model and numerical model is that the conceptual model pertains to the primarily qualitative information necessary to develop a conceptual understanding of the site, and the numerical model is the quantitative tool used to assess and support the conceptual model and to provide long-term prediction of plume conditions.

**Table 6**  
**Information and Data-Gathering Example and Data Relevance**

Question	Example Response	Relevance to Evaluation of Natural Attenuation as a Remedial Alternative
What waste-generating operations occurred at the site?	<ul style="list-style-type: none"> <li>• Steam and hot water washout of munitions</li> <li>• Explosive manufacturing operation</li> <li>• Range impact areas</li> <li>• Loading and packaging of munitions</li> <li>• Open burning/open detonation of munitions</li> </ul>	<ul style="list-style-type: none"> <li>• Identify contaminant sources</li> <li>• Identify contaminants</li> </ul>
How and when were wastes disposed?	<ul style="list-style-type: none"> <li>• Wastewater was collected in an impermeable sump and transported to an unlined lagoon for disposal from 1941 to 1949 and from 1952 to 1964</li> </ul>	<ul style="list-style-type: none"> <li>• Identify contaminant sources</li> <li>• Estimate potential duration and magnitude of release</li> </ul>
What is the status of the source of contamination?	<ul style="list-style-type: none"> <li>• The lagoon is not capped and no source material has been removed</li> <li>• The lagoon has been capped but source materials remain in place. The cap meets the requirements of an RCRA Subtitle C cap.</li> </ul>	<ul style="list-style-type: none"> <li>• Identify future contaminant release (direction, rate, and exposure pathways)</li> <li>• Estimate potential source loading</li> </ul>
What are the contaminants and what are their concentrations in affected media?	<ul style="list-style-type: none"> <li>• TNT</li> <li>• RDX</li> <li>• 2,4-DNT (support with available detailed analyses)</li> </ul>	<ul style="list-style-type: none"> <li>• Determine current risks</li> <li>• Obtain information for input into the transport model</li> <li>• Assess data quality and availability</li> </ul>
What are the possible pathways for contaminant migration?	<ul style="list-style-type: none"> <li>• Groundwater</li> <li>• Surface water</li> <li>• Air (through inhalation of dust)</li> </ul>	<ul style="list-style-type: none"> <li>• Perform assessment of risk</li> <li>• Identify potential receptors</li> <li>• Determine if threat is short term or long term</li> </ul>
Are there current or potential receptors?	<ul style="list-style-type: none"> <li>• The aquifer where the contamination exists is used for drinking water, but the contamination is currently 3.2 km (2 miles) upgradient from the drinking water wells.</li> </ul>	<ul style="list-style-type: none"> <li>• Determine whether there are current receptors that are impacted</li> <li>• Determine what receptors might be impacted in the future</li> </ul>
Has there been a change in concentrations of contaminants in groundwater over time?	<ul style="list-style-type: none"> <li>• The groundwater has been monitored over the past 5 years; during that time, the contaminant concentrations at the boundary of the plume have decreased to below detection limits.</li> </ul>	<ul style="list-style-type: none"> <li>• Determine whether natural attenuation has been occurring</li> <li>• Determine rate of plume expansion</li> <li>• Verify contaminant transport rates for the transport model</li> </ul>
Does the size and shape of the contaminated groundwater plume appear reasonable based on information gathered regarding the time and method of waste disposal?	<ul style="list-style-type: none"> <li>• The size and shape of the plume predicted from the site transport model and the actual plume do not agree. More field work needs to be performed to develop input parameters.</li> </ul>	<ul style="list-style-type: none"> <li>• Identify possible occurrence of natural attenuation to account for anomalies</li> <li>• Identify need for additional data to refine model input parameters</li> </ul>
What is the planned or likely future use of the site?	<ul style="list-style-type: none"> <li>• Industrial use after closure</li> </ul>	<ul style="list-style-type: none"> <li>• Identify and/or predict current and future receptors and evaluate risks to those receptors</li> </ul>
Who are the potential stakeholders of the remedial selection and implementation process?	<ul style="list-style-type: none"> <li>• Site Commander and Environmental Managers</li> <li>• Corps of Engineers</li> <li>• Federal Regulators</li> <li>• State Regulators</li> <li>• Citizens</li> <li>• Remedial Advisory Boards</li> <li>• BRAC Managers</li> </ul>	<ul style="list-style-type: none"> <li>• Identify requirements for further evaluation</li> <li>• Develop data requirements to address needs of stakeholders</li> <li>• Identify potential future uses of site</li> </ul>

<b>Table 7 Site Characterization Data</b>	
<b>Data Need</b>	<b>Relevance to Evaluation of Natural Attenuation as a Remedial Alternative</b>
<b>Background</b>	
Type of operations performed at the site (past and present)	Identify possible types of contaminants
Circumstances of release	Identify contamination source area(s) and how contaminant was released
Date of contaminant release	Predict migration of contaminant; identify possible attenuation over time
Estimates of contaminant mass/volume at release	Provide starting point for tracing migration or attenuation of contaminants
Groundwater monitoring data over time	Identify changes in groundwater flow rate and direction and associated trends of decreasing contaminant concentrations or migration of contaminant
Delineation of contaminant source	Identify specific source area for model development and/or future remedial needs Estimate contaminant mass and volume that will significantly influence the remediation time frame
Chemical characteristics of contaminant(s)	Identify contaminants and understand chemical characteristics that govern behavior in the subsurface
Physical characteristics of contaminant(s)	Understand physical characteristics that govern behavior in the subsurface
<b>Geologic and Hydrogeologic</b>	
Lithology of soils and aquifer matrix	Identify composition and structure of subsurface
Grain-size distributions	Subset of lithology that is used to assess contaminant transport rate
Depth to groundwater	Assess transport rates through the soil column and the attenuation caused by transport through the unsaturated zone
Hydrologic gradients	Quantify groundwater flow rate and direction
Aquifer permeability	Quantify groundwater flow rate and its variability across the site
Porosity and effective porosity	Quantify groundwater flow rate and retardation
Fluctuations in groundwater flow direction and velocity	Assess potential for changes in characteristics of contaminant plume
Fluctuations in groundwater elevations	Influence contaminant concentrations
Interactions between surface water and groundwater	The attenuation process may be significantly different in surface water than in groundwater. The interactions between the groundwater and surface water must be understood to understand the total effect on attenuation.
Meteorological and climatic information	Assess the impact on soil infiltration, evaporation rates, and groundwater recharge
<b>Geochemical</b>	
Dissolved oxygen	Contributes to the potential for biodegradation and other attenuation mechanisms
pH	Evaluate chemical and biological environment
Organic carbon content	Affects sorption, microbial degradation, and retardation rates
Adsorption coefficient ( $K_d$ )	Measure equilibrium partitioning
<b>Risks to Human Health and Environment</b>	
Locations of drinking water supplies	Identify potential receptors and determine the attenuation rates needed to protect receptors
Current and future receptors	Identify potential risks to human health and the environment and identify attenuation rates needed to ensure adequate protection
Current and future land use	Identify potential risks to human health and the environment and identify attenuation rates needed to ensure adequate protection
Human health risk assessment results	Identify attenuation rates needed to ensure adequate protection of human health
Ecological risk assessment results	Identify attenuation rates needed to ensure adequate protection of the environment

<b>Table 8</b> <b>Qualitative Input to the Preliminary Conceptual Model and Examples</b>	
Conceptual Information	Examples of Qualitative Data Used to Develop Conceptual Model
Hydrogeologic parameters	<ul style="list-style-type: none"> <li>• Infiltration</li> <li>• Natural flow boundaries</li> <li>• Surface conditions (streams, etc.)</li> <li>• Subsurface characteristics (geology, porous/fractured media, etc.)</li> <li>• Monitoring and delivery well locations</li> </ul>
Mode of chemical release	<ul style="list-style-type: none"> <li>• Lagoons used to hold munitions production wastewater over a period of many years</li> <li>• Open burning/open detonation activities</li> <li>• Land application of wastewater</li> </ul>
Amount of chemical released	<ul style="list-style-type: none"> <li>• Volumes released</li> <li>• Contaminant concentrations</li> </ul>
General behavior of the chemical in the environment	<ul style="list-style-type: none"> <li>• Chemical changes (transformation)</li> <li>• Sorption to soils</li> <li>• Biodegradation</li> </ul>
Lateral and vertical extent of contamination	<ul style="list-style-type: none"> <li>• Primarily within property boundaries</li> <li>• Contamination present down to bedrock</li> <li>• Limited offsite contamination</li> </ul>
General direction of contaminant migration through the environmental media of concern	<ul style="list-style-type: none"> <li>• Radially from the source</li> </ul>
Rate of contaminant migration through the environment	<ul style="list-style-type: none"> <li>• Rates of transport</li> <li>• Geology, geohydrology</li> </ul>

<b>Table 9</b> <b>Quantitative Input to Conceptual Model and Examples</b>	
Conceptual Information	Examples of Quantitative Data to Support the Conceptual Model
Hydrogeologic parameters	<ul style="list-style-type: none"> <li>• Number of subsurface layers</li> <li>• Hydraulic conductivity distribution</li> <li>• Water level elevation</li> <li>• Infiltration rates</li> </ul>
Mode of chemical release	<ul style="list-style-type: none"> <li>• Liquid or solid</li> </ul>
Amount of chemical released	<ul style="list-style-type: none"> <li>• Total mass</li> </ul>
Behavior of the chemical in the environment	<ul style="list-style-type: none"> <li>• Organic carbon partition coefficient</li> <li>• Biodegradation half life</li> </ul>
Lateral and vertical extent of contamination	<ul style="list-style-type: none"> <li>• Plume length</li> <li>• Plume width</li> <li>• Plume depth</li> </ul>
General direction of contaminant migration through the environmental media of concern	<ul style="list-style-type: none"> <li>• Three-dimensional direction of flow and mass transport</li> </ul>
Rate of contaminant migration through the environmental media of concern	<ul style="list-style-type: none"> <li>• Flow rate through soils</li> <li>• Flow rate in groundwater</li> </ul>

Ultimately, the conceptual model will assist in the following:

- Selecting a quantitative model and identifying data to be used in the model.
- Identifying current and future potential receptors (human and ecological).

***Nature, degree, and extent of contamination***

- What waste-generating operations occurred at the site?
- How and when were wastes disposed?
- How many and what kinds of source areas exist?
- Has the source(s) been removed?
- What are the contaminants, and what are their concentrations in affected soil and groundwater (degree and extent of contamination)?
- Is the plume well defined in three dimensions?
- Are multiple plumes present that diverge or coalesce?

***Potential receptors***

- What are the possible pathways for contaminant migration (e.g., soil, groundwater, surface water)?
- What is the planned or likely future use of the site?
- Are current or potential human or ecological receptors present?
- Are potential receptors of concern in the path of current groundwater flow direction?
- Based on the rate of contaminant migration, is there an immediate (1 year or less) or a long-term (more than 1 year) threat to receptors?

***Geologic and hydrogeologic setting***

- What is the topographic setting of the site?
- Where are the recharge and discharge areas?
- What is the general geology of the area?
- What are the lithologies of the soil and aquifer materials?
- What are the stratigraphic relationships, heterogeneity, and anisotropy?
- What are the hydraulic conductivities and how do they vary?
- What are the hydraulic gradients and how do they vary in magnitude and direction?
- What are the groundwater flow paths and velocities?
- What are the water-level fluctuations in wells at the site?
- Do potential preferential flow paths exist?
- What are the interactions between groundwater and surface water (gaining or losing streams)?

***Trends in contaminant concentration over time***

- What contaminant concentration data are available, and how extensive are these data?
- How reliable are the data?
- With what frequency do the data occur?
- Can a level of confidence be agreed upon by which to evaluate trends in the data?
- Have concentrations of contaminants in groundwater changed over time?
- Has the spatial or temporal distribution of contaminants changed over time?

- Do the changes suggest a shrinking or expanding plume relative to potential receptors? If so, can the rate of change be estimated?
- Do sampling points adequately define the flow paths of the contaminants?
- What is the variability in the data for a given location?
- Do water-level fluctuations correlate with concentration of contaminants?
- Are the sample locations along the groundwater flow paths?

#### ***Interested parties, or stakeholders***

- Who are the potential stakeholders of the remedial selection and implementation?
- Who are parties with interest in the future use of the site?

Answers to the questions above will provide a starting point to develop the site conceptual model described in Step 4. In addition, answers may provide a preliminary indication of the occurrence of, or potential for, natural attenuation at the site, thereby contributing to documentation in support of the first line of evidence (i.e., declining measurable contaminant concentrations and/or changes in contaminant distribution).

Depending on the degree to which the contaminated site has been investigated, much of the needed data and information may come from one or more of the following:

- Historical records.
- Remedial investigation (RI) reports.
- Risk assessment (RA) reports.
- Feasibility studies (FS).
- Preliminary assessment (PA).
- Site investigation studies (SI).
- Monitoring reports for existing remediation systems.
- Monitoring reports required for compliance.

A more complete list of potential sources that may be accessed to gather needed data and information is provided in Table 10.

## **Step 2. Evaluate existing data and conceptual model for evidence of natural attenuation**

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*Synopsis: This step involves the examination and use of the site characterization data and the conceptual model(s) developed in Step 1 to search for evidence of natural attenuation.*

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One justification of monitored natural attenuation in the context of EPA policy requires evidence of declining contaminant mass. Decreases in the concentration coupled with a shrinking distribution of the contaminant in the environment as reflected in existing site data are typically the simplest indicators of the occurrence of natural attenuation. These indicators may be observed directly through the examination of data that indicate that contaminant mass has decreased over time. Such observations require estimates of initial contaminant mass that can be compared with estimates of current and future contaminant



<b>Table 10</b>				
<b>Data Collection Information Sources</b>				
<b>Information Source</b>	<b>Type of Information</b>			
	<b>Historical</b>	<b>Geologic and Hydrogeologic</b>	<b>Geochemical</b>	<b>Risks to Human Health and the Environment</b>
EPA Files	•	•	•	•
U.S. Geological Survey		•		
U.S. Department of Agriculture (USDA), Natural Resources Conservation Service		•	•	
U.S. Department of Interior (DOI), Fish and Wildlife Agencies		•	•	•
DOI, Bureau of Reclamation	•	•	•	
U.S. Army Corps of Engineers	•	•	•	•
Federal Emergency Management Agency (for floodplain maps)		•		
U.S. Census Bureau				•
National Oceanic and Atmospheric Administration		•	•	
State Environmental Protection or Public Health Agencies	•	•	•	•
State Geological Survey		•		
State Fish and Wildlife Agencies				•
County or City Health Departments	•	•	•	•
Town Engineer or Town Hall	•			•
Local Chamber of Commerce	•			•
Local Airport				•
Local Library	•	•	•	•
Local Planning Boards				•
Local Well Drillers	•	•	•	
Sewage Treatment Plants	•			
Local Water Authorities	•	•	•	•
City Fire Departments	•			
Regional Geologic and Hydrologic Publications		•	•	
Court Records of Legal Action	•			•
Department of Justice Files	•			•
State Attorney General Files	•			•
Facility Records	•			
Facility Employees	•			
Citizens Residing Near Site	•			•
Waste Haulers and Generators	•			
Photographs	•	•		•
Hazardous Ranking Scoring (HRS) Package	•	•	•	•
Environmental Photographic Information Center	•	•		•
Source: Modified from EPA 1989.				

mass. These estimates are obtained from models based upon measured contaminant concentration and distribution and measured groundwater hydrology.

Once the initial models have been developed, the following questions should be answered:

- a. Can the risk to potential receptors be defined with the existing data concerning groundwater flow rate and direction and trends in contaminant concentrations?
- b. Are trends in contaminant concentration over time sufficient to support monitored natural attenuation, or must the second and/or third lines of evidence be pursued?

If, after developing the initial conceptual model with the available data, the evidence supporting the evaluation is inadequate as reflected in the responses to the two questions above, additional data requirements may be identified and the need for collection of new data justified. The new data can be used to enhance and refine the conceptual and numerical models and decrease the level of uncertainty or resolve unknowns.

### **Step 3. Develop numerical model(s)**

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*Synopsis: A site numerical model is developed to provide a basic understanding of site hydrogeology and contaminant transport. Numerical models provide the basis for evaluating past and future reductions in contaminant mass over time.*

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The numerical model is used to do the following:

- Estimate potential exposure concentrations.
- Estimate attenuation rates using actual data for calibration.
- Evaluate the potential effectiveness of various remedial alternatives.
- Assist in evaluating the effectiveness of “markers” that may be used to monitor the natural attenuation process.
- Identify additional data required and locations at which data should be collected.
- Develop theoretical predictions of attenuation that can be used in a comparison with actual data.

A list of model references and guidance documents is provided in Appendix C. Basic equations for evaluating transport through porous media are provided in Table 11.

As described earlier, natural attenuation of explosives occurs through one or more of the following mechanisms: microbial mineralization, transformation, and immobilization. These processes can be modeled by a numerical code, which simulates biological and/or chemical degradation, and sorption/immobilization. Many of the standard models contain simplified representations (linear adsorption/desorption, first-order decay, dilution) that may be

**Table 11**  
**Equations Used to Rapidly Assess Chemical Fate and Transport**

Property	Equation Used to Quantify Property	Input Parameter Description
Porosity	$\phi = 1 - \rho_d/P_d$	$\phi$ = total porosity $\rho_d$ = soil bulk density (M/V) $P_d$ = particle density (M/V)
Groundwater volumetric discharge (Darcy's Law)	$Q = KA(\Delta H/\Delta l)$	$Q$ = volumetric discharge (V/T) $K$ = hydraulic conductivity (L/T) $A$ = cross-sectional area of flow (L <sup>2</sup> ) $\Delta H$ = difference in hydraulic head at two measure points (L) $\Delta l$ = distance between two measure points (L)
Average linear groundwater velocity	$v = (K/\phi)(\Delta H/\Delta l)$	$v$ = groundwater velocity (L/T) $K$ = hydraulic conductivity (M/T) $\phi$ = aquifer porosity $\Delta H$ = difference in hydraulic head at two measure points (L) $\Delta l$ = distance between two measure points (L)
Steady-state radial flow to pumping well (confined aquifer)	$Q = 2\pi T\{(h-h_w)/[\ln(r/r_w)]\}$	$Q$ = well discharge (V/T) $T$ = aquifer transmissivity (L <sup>2</sup> /T) $r$ = distance from the pumping well (L) $r_w$ = well radius (L) $h_w$ = hydraulic head at the well (L) $h$ = hydraulic head at distance $r$ from the well (L)
Steady-state radial flow to pumping well (unconfined aquifer)	$Q = \pi K\{(h_o^2-h_w^2)/[\ln(r/r_w)]\}$	$Q$ = well discharge (V/T) $K$ = aquifer hydraulic conductivity (L/T) $r_o$ = distance of observations well from pumping well or distance at which drawdown is zero (L) $r_w$ = well radius (L) $h_w$ = hydraulic head at the well (L) $h_o$ = hydraulic head at distance $r_o$ from the well (L)
Contaminant retardation velocity	$v_o = \{v/[1+(\rho_b K_d/\phi_e)]\}$	$v_o$ = velocity $v$ = interstitial velocity in soil or water (L/T) $\rho_b$ = bulk mass density (M/V) $K_d$ = sorption coefficient (V/M) $\phi_e$ = effective porosity
Chemical distribution coefficient of organic compounds	$K_d = K_{oc}f_{oc}$ ( $f_{oc} > 0.1\%$ )	$K_d$ = distribution coefficient (V/M) $K_{oc}$ = organic carbon distribution coefficient (V/M) $f_{oc}$ = fraction of organic carbon in the soil or groundwater matrix
First-order biological decay	$C = C_o[\exp(-kt)]$	$C$ = chemical concentration (M/V) $C_o$ = initial chemical concentration (M/V) $t$ = time (T) $k$ = biodegradation rate constant (1/T)
Biological decay half-life	$t_{1/2} = (\ln 2)/k$	$t_{1/2}$ = half-life, the amount of time taken for 1/2 of the material to degrade $k$ = biodegradation rate constant (1/T) $\ln 2$ = natural logarithm of 2 = 0.693
First-order disappearance rate	$kt = \ln(C_o/C_t)$	$k$ = rate constant $C_o$ = initial chemical concentration (M/V) $C_t$ = chemical concentration at time $t$ (M/V)
Note: $M$ indicates units of mass, $T$ units of time, $L$ units of length, and $V$ units of volume (=L <sup>3</sup> ). Perform function within ( ) first, [ ] second, and { } last.		

sufficient to describe the processes occurring in some of the sites contaminated with explosives. For example, immobilization of TNT in a carbon-poor aquifer matrix may appropriately use the assumption of linear, reversible adsorption.

Groundwater models are available in three forms: coupled flow and transport, flow only, or transport only. Decoupled (flow only and transport only) numerical models are used to solve flow and transport problems separately.

The important aquifer properties to consider when selecting a computer model are as follows:

- Whether the medium is porous or fractured.
- Whether the aquifer is confined or unconfined and the associated storage properties (that is the specific storage and specific yield) and how they vary spatially across the site.
- The hydraulic conductivity (or transmissivity) of the medium and how conductivity varies spatially across the site.

The important aquifer boundary conditions to consider when selecting a computer model include the following:

- The presence and location of surface water bodies (e.g., rivers, streams, lakes, ponds, and oceans).
- Rainwater recharge rates.
- Evapotranspiration rates.
- Presence and location of impermeable zones.
- Presence and location of extraction/injection wells.
- Presence and location of drains.

With respect to calculating the fate and transport properties of a contaminant within the aquifer, the important factors in selecting a quantitative model are as follows:

- Initial concentrations to be used at the onset of the model run (e.g., current concentrations detected on the site).
- Source type (point source, line source, area source, or volume source).
- Mode of source release (constant or periodic over time).
- Modes of chemical transformation (biological degradation, abiotic chemical reactions).
- Aquifer properties such as dispersion (longitudinal, vertical, horizontal dispersivity).

The method the model uses for quantifying the various factors is very important and depends upon site conditions and the degree of certainty required from the model output. For example, when calculating the flow field, assigning a constant head (i.e., no change in the water elevation at a particular location) to cells within a model that represents a pond may be appropriate. In addition, when calculating the contaminant transport, representing a buried drum as a point source may be appropriate and a zone of soil contamination that leaches to the groundwater as an area source. Since information is typically gathered relatively slowly over time, selection of a quantitative model that has the most options for representing the various processes is prudent. However, the more

complex a model, the greater the time required to set up and run the model and, thus, the higher the associated costs.

Specific examples of model input parameters, methods for obtaining data that support these input parameters, and groundwater modeling results for an explosive-contaminated site are provided in Appendix D.

#### **Step 4. Collect additional data specific to natural attenuation of explosives**

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*Synopsis: This step identifies additional data requirements for determining the extent to which natural attenuation is occurring, identifying the mechanisms responsible, and improving predictive capabilities for natural attenuation over the long term. The needed data are collected through additional site characterization efforts and/or the conduct of laboratory tests.*

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New data may be required to enhance the decision-making process by providing the following:

- Additional, or more accurate, input for the numerical model.
- Direct evidence that attenuation is occurring at a sufficient rate (e.g., decreased contaminant mass over time).
- Indirect evidence of the potential for attenuation to be an effective remedy (e.g., site conditions are capable of supporting natural attenuation as a remedy).

New data may be acquired through onsite monitoring followed by sampling and analysis and/or by conducting laboratory studies with sampled material. These activities are described below.

##### ***Groundwater monitoring***

Existing groundwater data may be insufficient due to any one or more of the following:

- Placement of wells relative to the plume and/or potential receptors.
- Infrequent or insufficient number of sampling events.
- Significant inexplicable variability and absence of trends.
- Limited or inadequate list of analytes.
- Insufficient delineation of regional flow for definition of model boundary conditions.

If the groundwater plume lacks sufficient definition, installation of new wells should be considered (Driscoll 1986) (See Appendix B). As a minimum, the plume should be defined in all four cardinal directions and vertically. Data must also be sufficient to define groundwater flow direction(s) and rate(s).

Although three data points can define a trend in contaminant concentration over time, several years of data will improve the confidence in the trend. Since fate processes of explosives are typically slow, long-term data are desirable. For

example, if existing data are unusable, an extended groundwater monitoring plan (e.g., covering 2 to 5 years) is advisable. The frequency of sampling can be based upon the site hydrologic flow dynamics. In a rapidly moving system, quarterly sampling for 2-5 years may adequately demonstrate trends. In a sluggish system, annual or semiannual sampling for 10 years, or longer, may be appropriate.

Variability in contaminant concentration data can be minimized by ensuring that (a) the sampling protocol is followed consistently for each well in each sampling event; (b) the well is adequately purged of the influence of oxygen at the well-head before a sample is taken; (c) Teflon sampling tubing is dedicated to each well to minimize retention of the analyte by the tubing and to prevent cross-well carry-over of contaminants; (d) one of every ten samples is analyzed in duplicate; (e) well sampling order is established from lowest to highest contaminant concentration to minimize carry-over; and (f) pump is decontaminated between wells, and random checks for contaminants in the rinsate are conducted for each sampling round.

The selection of analytes will affect the utility of groundwater and soil data. Due to the slow rate of microbial degradation of explosives that is typical in soils and aquifers, few geochemical markers are available to provide evidence of natural attenuation. The oxygen status (i.e., dissolved oxygen, or redox potential) may suggest whether aerobic or anaerobic processes are possible. For example, if the aquifer is anaerobic and sufficient carbon and other nutrients (e.g., nitrogen and phosphorus) are present to support cometabolic microbial activity, RDX mineralization may be significant. Therefore, monitoring dissolved oxygen, redox, and organic carbon is advisable. If TNT is present in soils or groundwater, monitoring for TNT transformation products will provide evidence of changes in the parent compound. Presence of the transformation products in soils containing high organic carbon content suggests potential for immobilization by covalent bonding to functional groups on the organic matter. Since clay content increases sorption capacity and is believed to contribute to transformation and immobilization processes, analysis of particle-size distribution (percent sand, silt, and clay) is warranted.

### ***Cone penetrometry***

When data obtained from groundwater monitoring wells are insufficient to adequately define (a) the extent of the contaminant plume or (b) the site hydrogeology, cone penetrometry (CPT) sampling may be helpful (Booth, Durepo, and Temet 1993; Schroeder, Booth, and Trocki 1991) (See Appendix B). CPT can refine hydrogeology and provide lithological profiles of the site. By collecting discrete samples at various depths, contaminant distribution can be refined and the definition of the plume in the conceptual model improved. Furthermore, subsurface soil and aquifer material can be collected for tests in support of the second and third lines of evidence for natural attenuation.

## *Evaluating the potential for adsorption and transformation*

Two of the key processes involved in estimating site capacity for explosives are sorption and transformation of explosives by aquifer soils. Sorption results in a nondestructive lowering of groundwater concentrations. Transformations result in changes in the chemical characteristics of the contaminants to new chemical species. These processes are key to determining the potential for removal of a significant mass of the parent compound and/or transformation products. The capacity for adsorption and transformation can vary considerably across a site; therefore, evaluating the potential for these processes is essential. Evaluating the potential for adsorption and transformation requires collection and testing of aquifer soil and groundwater from the site ("I. Soil and water for testing" discussed below and in Appendix B). Site characterization, including lithological profiles, and measuring adsorption and transformation rates and extent with representative aquifer soils is necessary. Pseudo-first-order kinetics, which indicate the half-life of the contaminant of interest ("II. Determinations of transformation rates and sorption kinetics" discussed below), and the adsorption coefficients, which indicate the affinity of site soil for the contaminant and its leaching potential ("IV. Determination of adsorption coefficients" discussed below), can be used to refine model input parameters. Model input parameters include rate constants and half-life ("III. Calculations of rate constants and half-life" discussed below) and partition coefficients ("IV. Determination of adsorption coefficients" discussed below).

Laboratory-measured rate coefficients for use in groundwater models may require adjustment to accurately reflect field conditions. Typically, laboratory tests tend to overestimate degradation or immobilization potential attainable in the field. This is partially due to the fact that laboratory tests are conducted under optimal conditions for efficient contact between reactants, while both contaminants and reactive surfaces are typically more heterogeneously dispersed in the aquifer. Furthermore, laboratory tests measure processes occurring in relatively short time frames that must be extrapolated to long-term end points by predictive modeling and extended monitoring. Laboratory data should be interpreted in the context of site-specific distribution of contamination, site lithological heterogeneities, and groundwater flow parameters.

- I. ***Soil and water for testing:*** After the principal soil types in an aquifer have been identified by geophysical investigations (See Appendix B), a sufficient soil sample for all tests (2-3 L of each type of soil identified) is collected and stored in a sealed container at 4 °C until mixed and used in tests. To preserve the soil physical characteristics sieving of soil prior to testing should be confined to removal of gravel >2 mm in nominal diameter (No. 10 sieve). Water from groundwater monitoring wells on the site is also collected in sufficient quantity for all tests using established protocols (See Appendix B) and stored at 4 °C until used. If contaminant levels are high, the groundwater is used undiluted for the highest concentration tests and diluted with clean groundwater of similar chemical characteristics to obtain lower concentrations. If contaminant

levels in site groundwater are low, the contaminants of interest must be added to the water to achieve the desired test concentrations.

- II. ***Determinations of transformation rates and sorption kinetics:*** The tests are conducted in batch by shaking and/or in columns. Concurrent batch and column tests for TNT sorption and disappearance rates with LAAP aquifer soils showed close agreement (Pennington et al. 1999a). Procedures for batch testing are standard and available in 40CFR796.2750 (<http://frwebgate.access.gpo.gov/cgi-bin/multidb.cgi> at 40CFR796.2750-- Sec. 796.2750 sediment and soil adsorption isotherm). Column test procedures and interpretation are presented in Myers et al. (1998).

Studies are conducted under either aerobic or anaerobic conditions, whichever is prevalent in the aquifer. Oxygen status of the groundwater is determined by taking dissolved oxygen readings on an in-line monitor after removal of three well volumes of groundwater or after dissolved oxygen readings stabilize. Aerobic conditions exist in the aquifer when dissolved oxygen is present ( $Eh \geq 330$  mV) (Turner and Patrick 1968) according to the in-line flow meter readings at the monitoring well. Anaerobic conditions ( $Eh \leq 330$  mV) exist when no dissolved oxygen is present. During batch testing, groundwater and aquifer soil are used in a water:soil ratio of 4:1. Either the same solution is sampled over time by removing a completely mixed subsample, or separate tests are sacrificed for each sampling time. Conducting the tests under anaerobic conditions requires maintaining anaerobic conditions during all steps in the test (Price et al. 1997; Brannon, Price, and Hayes 1998). The separated (by centrifugation) aqueous phase is preserved with 1.5 g sodium bisulfate/L, refrigerated at 4 °C, and analyzed for the full range of explosives contaminants, which include TNT, RDX, HMX, tetryl, 1,3,5-trinitrobenzene (TNB), 1,3-dinitrobenzene (DNB), 3,5-dinitroaniline (DNA), 2,6-dinitrotoluene (2,6DNT), 2,4-dinitrotoluene (2,4DNT), 4-amino-2,6-dinitrotoluene (4ADNT), 2-amino-4,6-dinitrotoluene (2ADNT), 3,5-dinitroaniline (DNA), 2,6-diamino-4-nitrotoluene (2,6DANT), 2,4-diamino-6-nitrotoluene (2,4DANT), 4,4',6,6'-tetranitro-2,2'-azoxytoluene, 2,2',6,6'-tetranitro-4,4'-azoxytoluene, hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX). The analytical method is EPA Method 8330 (EPA 1994b).

All practicable operations are conducted in the dark to avoid photodegradation of the analytes. Calculations of equilibration time for sorption tests are determined according to the guidelines given in 40CFR796.2750. Most explosive compounds reach steady state within 24 hr with aquifer soils (Pennington et al. 1999a), making equilibrium partitioning an appropriate assumption.

Adsorption and transformation kinetics are calculated as follows: the initial concentration,  $c_0$ , is divided by the analyte concentration,  $c$ , for



each sampling time,  $t$ . The natural logarithm of these values,  $\ln(c_0/c)$ , is regressed (y-axis) against time (x-axis) in hours. The slope of the regression is the first-order rate constant,  $k$ , used in the half-life calculations below.

- III. **Calculations of rate constants and half-life:** Removal rate constants for explosives contaminants in solution can be expressed by pseudo first-order kinetics that take the form

$$dc/dt = -kc \quad (1)$$

where

$c$  = chemical concentration of reacting substance

$k$  = pseudo first-order reaction constant

$t$  = time

Pseudo first-order kinetics reduces to the equation

$$\ln(c_0/c) = kt \quad (2)$$

where  $c_0$  is the concentration of the reacting substance at time 0. Once a value of  $k$  is obtained, the half-life period of the reacting substance,  $t_{1/2}$ , can be calculated using the equation

$$t_{1/2} = \frac{0.693}{k} \quad (3)$$

- IV. **Determination of adsorption coefficients ( $k_d$ ):** Testing should be conducted using freshly obtained groundwater and aquifer soil using the general procedures outlined in 40CFR796.2750. Use solutions containing six different concentrations of contaminant in a 4:1 water:soil ratio. A suitable test size consists of 4 g of soil (oven-dry weight basis). Solutions are prepared from contaminated groundwater diluted to desired concentrations with contaminant-free groundwater or uncontaminated groundwater spiked with the contaminants of concern. The mixtures are shaken until the previously determined equilibrium time is reached. After centrifugation following guidance given in 40CFR796.2750, the aqueous phase is removed and analyzed for contaminants of interest. Calculations are described in the CFR. Column tests (Myers et al. 1998; Pennington et al. 1999a) provide an alternate means of estimating sorption and transformation of explosives by aquifer soils. Analysis of breakthrough curves for explosives during column tests can also provide a measure of irreversible adsorption or immobilization of explosives by the aquifer soil.

Typically, TNT and RDX have relatively long half-lives in aquifer compared with surface soils due to the limited amount of organic carbon in aquifer soils. For example, at Louisiana Army Ammunition Plant (LAAP), the half-life of TNT ranged from 21.4 to 50.4 days in aquifer soil, whereas, values of 0.5 to 2 days are typical in surface soils. Adsorption coefficients also tend to be lower in aquifer than in surface soils. Typical surface soil  $K_d$  values for TNT and RDX range from 0.58-11 and 0.21-0.33 L kg<sup>-1</sup>, respectively, whereas  $K_d$  values for aquifer soils at LAAP were 0.04-0.27 and 0.27-3.5 L kg<sup>-1</sup> for TNT and RDX, respectively. If site soils are very low in organic carbon (<0.1 percent) and high in sand (>90 percent), the  $K_d$ s can be assumed to be zero for model input. If the soils are higher in organic carbon and/or high in clay or silt content, the assays should be conducted.

### *Evaluating the potential for microbial degradation*

The conditions necessary for microbial degradation of explosives in situ are incompletely understood. Reduction of TNT to amino transformation products can occur under both aerobic and anaerobic conditions. Subsequent immobilization of transformation products is favored by (a) the presence of organic carbon, which can serve as a co-metabolite for microbial degradation and as a substrate for covalent binding, (b) the presence of Fe<sup>0</sup>, Fe<sup>+2</sup>, and HS<sup>-</sup> under reducing conditions, (c) the presence of high cation exchange capacity (CEC), and (d) high pH (>7.5). Mineralization has been observed with specific microbial isolates and at extremely reducing conditions (-200 mV, Preuss and Rieger 1995, Funk et al. 1993), but not in situ. However, mineralization of radiolabeled TNT and RDX by aquifer microflora has been observed (Pennington et al. 1999a). Microbial degradation of RDX is favored under reducing conditions. The potential for microbial degradation can contribute to a weight-of-evidence for natural attenuation as a remedial alternative and can be indirectly evaluated by examining soil characteristics that regulate microbial habitats. Examples of such characteristics and possible interpretations are presented in Table 12. A summary of how this information can be used to evaluate the potential for microbial degradation is shown in the following example.

An evaluation of surface and subsurface soil environments at LAAP yielded results that provide some predictive capability of the potential for biological degradation of explosives. **Surface soils** were low in organic carbon, total phosphorus, and nitrate-nitrogen; loamy to silty in texture; and were mildly acidic (pH value of 5.0 to 5.5). These parameters are expected to support moderate activity by both bacteria and fungi, but population levels are expected to be well below those of more fertile mineral soils having organic matter levels of 1 to 3 percent at a neutral pH. Sufficient fine-grained material exists in the surface soils to provide for abundant microbial growth on the soil particles. Low values for nitrogen and phosphorus in the surface soils suggest that the inorganic components of these materials are moving to the subsurface upon release from decomposing plant material. **Subsurface soils** were primarily mildly acidic (pH values ranging between 5.0 and 7.0 depending on depth). These soils had a sandy loam to loamy sand texture, very little clay, high levels of total phosphorus, and

**Table 12**  
**Soil Characteristics That Regulate Microbial Habitat**

Factor	Characteristics	Correlation to Potential for Natural Attenuation of Explosives
Soil texture - sand content	Low surface area is available for microbial colonization.	As the sand content increases, potential for growth and maintenance of microbial populations necessary for degradation decreases.
	Sand is inert with little potential for interaction with microbial nutrients or explosives.	Sand will not inhibit microbial access to explosives and will not compete with explosives for microbes. Since sand does not hold inorganic nutrients or dissolved organic carbon, microbial growth is limited in sand.
	Greater porosity and lower organic carbon results in lower oxygen demand and higher oxygen levels. The higher porosity also increases movement of air through soil.	The presence of sand can enhance oxygen availability for microbes.
Soil texture - silt content	Silt exhibits a greater surface area than sand for microbial colonization.	As silt content increases at the expense of sand, potential for growth of necessary microbial populations increases.
Soil texture - clay content	Clay exhibits a very high surface area for microbial attachment. However, low porosity can limit permeability and reduce available nutrients and oxygen.	The presence of clay will provide a greater potential for growth and maintenance of microbial populations than sand and silt alone.
	Clays have a relatively high affinity for TNT.	Higher clay content may inhibit microbial access to TNT thus reducing the potential for degradation.
Organic content of soil	The organic portion of the soil contains nutrients necessary for microbial colonization.	A low organic carbon content suggests that the soil may lack the ability to support microbial populations necessary for degradation.
Inorganic nutrient content of soil	Sufficient levels of nitrate, ammonium, and phosphate are essential for microbial colonization.	Water-soluble nitrogen and phosphorus are necessary to maintain a microbial habitat in soils. Low levels indicate decreasing potential for the maintenance of adequate habitats.
Soil pH	Soil pH regulates the abundance and diversity of microorganisms.	Extremely acid (pH < 3) or alkaline (pH > 9) soils can inhibit the growth of many kinds of bacteria. However, fungi may be dominant at pH values between 2 and 3.

extremely low levels of organic carbon. Subsurface nitrate-nitrogen levels were slightly higher than those in the surface soils. The pH levels and levels of nitrogen and phosphorus in the lower depths were more supportive of microbial activity than the values for these components in the surface soils. However, the lack of available surfaces for microbial colonization (i.e., low clay content) and the low levels of organic carbon suggested that these environments were capable of sustaining only very low microbial populations and, in general, very little microbial activity was expected. Results of microbial studies verified conclusions reached by examining these site characteristics.

## Data Examples

Soil	pH	%Sand	%Silt	%Clay	Total P mg kg <sup>-1</sup>	%OC	Total N mg kg <sup>-1</sup>	NO <sub>3</sub> -N mg kg <sup>-1</sup>	NH <sub>4</sub> -N mg kg <sup>-1</sup>	CEC meq 100 g <sup>-1</sup>
Surface	5.2	39.7	45.1	2.5	5	0.20	ND*	4.8	ND	5.5
Surface	5.4	34.7	51.7	13.7	2	0.25	ND	2.4	ND	6.1
Subsurface	5.4	61	21	18	432	0.12	716	6	2	ND
Subsurface	6.4	89	3	8	482	0.14	615	8	4	ND

Note: ND = not determined.

A more detailed and quantitative approach to assessing microbial degradation potential may be taken by use of tests conducted on surface soil samples and/or on subsurface samples taken with CPT as described in Appendix A. A soil mineralization radioassay can be used to evaluate the microbial degradation potential of the site. Test results provide evidence that site microorganisms are *capable* of functioning in the natural attenuation of explosives. The radioassay demonstrates the presence or absence of explosives mineralization activity in site soils and estimates mineralization rates.

Positive results of soil mineralization radioassays constitute indirect evidence of microbial degradation as a mechanism of natural attenuation of explosives at the site. The test requires that 30 percent (w/v) slurries of soils freshly obtained from the field be challenged with <sup>14</sup>C-acetate, <sup>14</sup>C-TNT, <sup>14</sup>C-RDX, or other contaminants of interest. The slurries are examined for their rate of <sup>14</sup>CO<sub>2</sub> production. The results provide (a) predictions of the rate and extent of explosives mineralization occurring at a specific location, and (b) a relative indication of the viability of the biomass at the site. This test must be conducted in a laboratory licensed for handling radioactive materials by the Nuclear Regulatory Commission. Details of the procedure are provided in Appendix A.

Promising new tests that potentially support monitoring of natural attenuation processes of explosives include lipid biomarker analyses for estimating in situ microbial biomass and nucleic acid biomarker analyses for detecting genes encoding enzymes required to catalyze specific degradation processes. These tests were applied to explosives in surface and subsurface soils at LAAP (Pennington et al. 1999a,b) and at Joliet Army Ammunition Plant (Pennington et al. 1998a). Results were promising.

## Step 5. Inform stakeholders and coordinate further evaluation<sup>1</sup>

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*Synopsis: This step provides for coordination with regulators and other stakeholders. Recommended coordination includes presentation of the current understanding of the potential for monitored natural attenuation as a protective remedial alternative at the site. Related discussions between the evaluator and stakeholders will provide guidance for further evaluation and implementation and will familiarize the evaluator with Federal, State, and local policies and attitudes regarding the selection and the implementation of monitored natural attenuation.*

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The experience of Federal, regional, and State regulators with monitored natural attenuation may be based upon contaminants such as chlorinated solvents and petroleum hydrocarbons. The evaluator must be able to provide all stakeholders with technical justification for monitored natural attenuation of explosives.

**Presentation of information.** A presentation of the feasibility of monitored natural attenuation at the site for the regulatory community should include the following:

- **Background technical information.** This information should focus on the ways and extent to which explosives are mobile in the environment and the mechanisms involved in their attenuation. Based on the results of recent research, specific natural attenuation mechanisms to be described include immobilization of TNT and degradation of TNT and RDX.
- **Site-specific conceptual model.** This model will provide an overall qualitative picture of the site describing contamination sources, contaminant migration pathways, and potential receptors.
- **Numerical/computer model.** Quantitative/computer modeling will predict the potential for monitored natural attenuation to be protective of receptors.
- **Generation of data for model.** To provide for the most accurate predictive capability offered by the computer model(s), additional field data and/or laboratory tests may be required.
- **Results of the model.** Depending upon the availability of data and information and the progress made in applying the computer model(s), results may be presented regarding the feasibility of selecting monitored natural attenuation as a remedy for the site.

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<sup>1</sup> This step may be required at any point in the evaluation. Its presence here is based on the desirability of having a good understanding of the site and of monitored natural attenuation as developed in Steps 1 through 4 prior to presentation and coordination.

- **Data quality and sufficiency.** A consensus should establish what will constitute adequate and acceptable data and a reasonable timeframe to achieve remediation goals. The EPA Guidance (EPA 1999) states the following concerning data quality:

“For environmental decision-making, data must be of adequate quality and usability for their intended purpose, the level of confidence on calculated attenuation rates should be documented- statistical confidence intervals should be estimated, sensitivity analyses should be performed to determine dependence of calculated remediation timeframes on uncertainties in rate constants and other factors.”

According to EPA guidance a “reasonable timeframe” is as follows (EPA 1999):

- “- A reasonable timeframe is one that is comparable to that which could be achieved through active remediation
- The most appropriate timeframe must be determined through analysis of all appropriate remedy alternatives
- For restoration of groundwaters to beneficial uses, a comparison of restoration alternatives from most aggressive to passive is necessary to establish the range of time required to achieve remediation objectives
- A measured decrease in contaminant concentrations of **at least one order of magnitude** is necessary to determine an appropriate rate law to describe rate of attenuation, and to demonstrate that the estimated rate is statistically different from zero at the **95% level of confidence.**”

- **Implementation considerations.** The implementation of monitored natural attenuation will require a long-term monitoring program to ensure that monitored natural attenuation is achieving the remedial objectives and that contamination is not threatening receptors. The presentation to the regulators should describe the use of sentinel wells to achieve monitoring objectives. The presentation, in turn, can provide the basis for discussions to identify potential numbers and locations of any proposed new wells.
- **Contingencies.** A plan for implementing monitored natural attenuation must include contingency remedial actions to be taken in the event that monitored natural attenuation is not effective or is no longer capable of achieving remedial objectives. Possible contingencies to be implemented at the site should be presented. This presentation can provide the basis for subsequent discussions relating to contaminant concentrations that would “trigger” the implementation of a contingency and the types of contingencies that may be most appropriate. The development of contingencies is addressed in Step 10 of this protocol.

The presentation should inform as well as provide a basis for discussions of subsequent evaluations of natural attenuation and other alternatives, if appropriate. Specific topics of discussion may include the following:

- Remedial objectives.
- Future site use.
- Number and location of sentinel wells.
- Monitoring requirements.
- Contaminant concentrations detected in sentinel wells that would trigger requirements for the implementation of contingency measures.

The outcome of these discussions may result in revisions or refinement of the scope of the evaluation of monitored natural attenuation and may require revisions to the site conceptual and quantitative models.

## **Step 6. Refine the site conceptual and numerical models**

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*Synopsis: The original conceptual and numerical models will be refined by use of new data acquired in Step 3. Refinement of these models will enhance the capability to assess the presence of natural attenuation and predict its progress.*

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The procedure for this step includes the following:

- a. Compiling and evaluating field and/or laboratory data to support monitored natural attenuation and reduce the uncertainty associated with results based on previously gathered information.
- b. Modifying the conceptual model as necessary to reflect new data and information (e.g., changes in locations of "hot spots," changes in flow and transport directions).
- c. Recalibrating computer model(s), if warranted, with the additional data.
- d. Quantifying results using the computer model(s).
- e. Conducting sensitivity analysis, which consists of varying data or computer model input parameters within their range of potential values and documenting the change produced in the result.

The selected computer model may prove to be inadequate in light of the new data, and another computer model may be selected.

## **Step 7. Assess feasibility of monitored natural attenuation**

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*Synopsis: A review of all of the available data together with the revised models will permit assessment of the feasibility of monitored natural attenuation and the time required to achieve the desired remedial objectives.*

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At this stage in the process, sufficient data should be available upon which to base decisions regarding the feasibility of using monitored natural attenuation at the site. However, if the uncertainty remains high, additional data may be required (i.e., return to Step 3). All decisions must be well supported by quantitative and qualitative documentation generated during the previous steps.

An important aspect of this step is the quantification of uncertainties. This includes calculating various statistical parameters to assess the significance of the results and identifying the sensitivity of calculations to certain input parameters used in computer models. (See Appendix D.)

A sensitivity analysis provides a measure of how data uncertainty affects the outcome of a calculation, or essentially, how certain one can be about a particular decision. In its simplest form, a sensitivity analysis consists of varying an input parameter between two values and noting the difference in the outcome of the calculation. As can be imagined, the sensitivity analysis can become quite complex if one is interested in the sensitivity of the outcome of a complex computer model to a variety of different input parameters, each of which is dependent upon the other. Most commonly, even if a complex computer model is used to assess the feasibility of monitored natural attenuation, the sensitivity analysis will consist of keeping all input parameters constant and individually varying each parameter within its most likely range of values.

Once the uncertainty and sensitivity of the data and calculations have been assessed, various conclusions regarding the feasibility should be developed. These conclusions should be presented in the context of their reliability. This can be done, for example, by expressing the confidence limits (See Appendix E).

## **Step 8. Evaluate protectiveness of monitored natural attenuation for human health and the environment**

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*Synopsis: This step integrates results of Steps 1 through 7 to determine if monitored natural attenuation can meet the evaluation criterion of adequately protecting human health and the environment.*

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A threshold criterion in the evaluation of remedial alternatives is the ability of a given alternative to adequately provide for the protection of human health and the environment. To address this criterion, information developed in the preceding steps are used together with factors affecting risks to ensure protection of potential receptors.

An exposure pathway analysis is performed to determine the ability of monitored natural attenuation to adequately reduce current and future risks to human or ecological receptors. The focus of this analysis is to determine whether the presence or movement of the contaminants of concern (as predicted in the refined site models) results in actual or potential exposures to receptors that present unacceptable risks. To accomplish this, consider the following:

- Land use, current and future.
- Groundwater use, current and future.
- Point(s) of exposure, current and future.
- Timeframe.

Factors to be evaluated for each of these considerations are presented in Table 13.



**Table 13**  
**Exposure Evaluation Factors**

Element	Evaluation Factor
<b>Land use</b> <i>Includes current and reasonably potential future uses of site and surrounding properties</i>	<ul style="list-style-type: none"> <li>• Current land use of the site</li> <li>• Current land use of properties adjacent to the site</li> <li>• Current zoning or planning designation for the site</li> <li>• Current zoning or planning designation for surrounding properties</li> <li>• Reasonably potential future land use of the site using the duration of exposure as the maximum time into the future to evaluate</li> <li>• Reasonably potential future land use of the surrounding properties using the duration of exposure as the maximum time into the future to evaluate</li> </ul>
<b>Groundwater use</b> <i>Includes current and reasonably potential future quality and potential use of ground water as a drinking water source</i>	<ul style="list-style-type: none"> <li>• Existing classification of affected groundwater by State</li> <li>• Setting (e.g., urban, rural, industrial)</li> <li>• Yield rates of aquifer</li> <li>• Existing groundwater quality (naturally occurring and ambient)</li> </ul>
<b>Receptors, or points of exposure</b> <i>Includes actual and potential points of exposure</i>	<ul style="list-style-type: none"> <li>• Actual or known location of current or future receptor</li> <li>• Anticipated future receptors</li> </ul>
<b>Time frame</b>	<ul style="list-style-type: none"> <li>• Predicted time to reach receptor without attenuation</li> </ul>
Source: Adapted from Rocco (1997).	

### **Step 9. Compare monitored natural attenuation to other alternatives using established evaluation criteria**

*Synopsis: This step will complete the determination of the feasibility of monitored natural attenuation based on criteria established by EPA for the evaluation of remedial alternatives.*

In the analysis of remedial alternatives, a determination of feasibility and a comparison between alternatives may be accomplished by examining the response of each alternative to a set of criteria (as described in Chapter 2). Some factors to consider in evaluating monitored natural attenuation against these criteria are presented in Table 14. For a description of the criteria, refer to Figure 4.

Alternatives may be based on a single process (i.e., natural attenuation alone) or may include a battery of processes in which monitored natural attenuation plays a role. With respect to the criteria shown in Table 14, the alternatives should be evaluated as a whole system.

A range of possible contingency remedies exist for sites contaminated with explosives. These include in situ and ex situ physical, chemical, and/or biological processes. A comprehensive summary of potential remedial alternatives for explosive-contaminated sites is provided in the Federal

**Table 14**  
**Criteria for Detailed Analysis of Monitored Natural Attenuation**

Criterion	Factors to Consider When Evaluating Natural Attenuation
Overall protection of human health and the environment	<ul style="list-style-type: none"> <li>• See results of Step 8 of protocol and factors below</li> </ul>
Compliance with Applicable or Relevant and Appropriate Requirements (ARARs)	<ul style="list-style-type: none"> <li>• Compliance with ARARs will be site specific.</li> <li>• Compliance may be affected by how various State agencies view natural attenuation.</li> </ul>
Long-term effectiveness and permanence	<ul style="list-style-type: none"> <li>• Performance monitoring will be required when implementing natural attenuation to demonstrate that natural attenuation effective, to detect contaminant migration or new releases, and to verify the attainment of cleanup objectives. Performance monitoring is required as long as contamination levels remain above required cleanup levels at points of compliance.</li> <li>• Long-term liability may be of concern.</li> </ul>
Reduction of toxicity, mobility, and volume through treatment	<ul style="list-style-type: none"> <li>• Natural attenuation is not a "no action" alternative and may be considered a passive treatment alternative incorporating one or more attenuating mechanisms.</li> <li>• The specific attenuating mechanism(s) involved will affect the ability of the alternative to result in the destruction of hazardous materials; the reduction in toxicity, mobility, and volume of hazardous materials; and the irreversibility of the process.</li> <li>• Typically, fewer wastes are generated than during active remediation.</li> </ul>
Short-term effectiveness	<ul style="list-style-type: none"> <li>• Longer time frames may be incompatible with future land uses.</li> <li>• Length of time required for natural attenuation to achieve cleanup levels should be compared with the times required for other alternatives.</li> <li>• Less disruption of the environment during remediation is required.</li> <li>• Little threat is posed to the community or workers by remedial action.</li> </ul>
Implementability	<ul style="list-style-type: none"> <li>• Natural attenuation may be easier to use in comparison with engineered remediation technologies (note: this does not imply "easier to implement").</li> <li>• No equipment downtime is involved.</li> <li>• Appropriate monitoring points must be accessible.</li> </ul>
Cost	<ul style="list-style-type: none"> <li>• Costs associated with site characterization requirements may be significant.</li> <li>• Costs associated with long-term performance monitoring may be greater than for active remedial alternatives at some sites.</li> <li>• Indirect costs (e.g., reduced land value, restricted land use, liability, legal costs) may be associated with natural attenuation over the long term.</li> </ul>

Remediation Technologies Roundtables' Remediation Technologies Screening Matrix and Reference Guide, 3rd Edition.<sup>1</sup>

### Step 10. Finalize long-term monitoring and contingency plans

*Synopsis: The successful implementation of monitored natural attenuation as a remedial alternative must include a comprehensive plan that addresses the long-term management of the site to ensure that human health and the environment are adequately protected. This step describes some of the primary issues that must be addressed in preparing for implementation and contingencies.*

<sup>1</sup> This document was prepared by the Army Environmental Center (Report No. SFIM-AEC-ET-CR-97053) and is available on line at <http://www/frtr.gov/>. Paper copies may be ordered from the National Technical Information Service at (703) 487-4650.

Goals must be established for achieving specific reductions in contaminant mass within a timeframe that is protective of receptors of concern. These goals can be based upon regulatory requirements and the expected attenuation rates as conceptualized in the developed models. The plan for implementing monitored natural attenuation must focus on achieving these goals and should include the following:

- Monitoring
- Long-term protectiveness
- Contingencies

**Monitoring.** Long-term monitoring will be required to confirm the effectiveness of monitored natural attenuation as a remedial action and to ensure protection over time. Monitoring can also provide empirical verification of modeling results. Monitoring will include groundwater sampling and analysis and may, depending upon the site and regulatory compliance requirements, include surface water, sediments, and soil sampling.

The monitoring program will address the following objectives (EPA 1999) (flowchart references given in parentheses, Figure 11, Sheet 5):

- Demonstrate that natural attenuation is occurring according to expectations (process performance).
- Determine if a plume is expanding (decreasing contaminant mass).
- Ensure that no receptors are impacted (receptor protection).
- Detect new releases that could negatively impact the course of natural attenuation (new releases).
- Demonstrate that measures implemented to protect potential receptors remain effective (mechanism performance).
- Detect any changes in environmental conditions that may affect natural attenuation processes (changes in environmental conditions).
- Verify attainment of cleanup objectives (cleanup objectives attained).

The monitoring plan should describe the locations and use of sufficient monitoring wells to do the following:

- Detect further migration of the plume.
- Provide data on overall plume behavior and trends in concentrations within the plume over time and distance from the source.
- Detect changes in background water quality and environmental conditions.
- Detect changes in groundwater flow patterns.

Monitoring of groundwater (and surface water under some conditions) will be required to track changes in the behavior of the contaminant plume and to monitor for continued protection of potential receptors. Development of an effective monitoring program requires placement of monitoring wells appropriately to ensure adequate plume definition over time and sampling with sufficient frequency to detect any shifts in contaminant location and direction of movement. Consideration must be given to the number and locations of monitoring wells and to groundwater flow rate and direction over time. Characterization of the site hydrology, geology, and contaminant distribution is

critical. For example, a typical remedial monitoring scheme may require the installation of one upgradient well and three downgradient wells. For the implementation of monitored natural attenuation, this number is likely to be increased to include at least one well close to the contamination source and others along the center of the contaminated plume and around the outer boundary of the plume as shown in Figure 12 (EPA 1994a). At least one sentinel well will also be needed between the plume and the potential receptor(s). As monitoring continues over time, the representativeness of the suite of wells must be reevaluated. For example, if the plume is moving as it shrinks, installation of new wells and dropping of old wells may be necessary. Wells that achieve the cleanup level may be candidates for discontinued monitoring. Wells must be monitored until cleanup goals are attained.

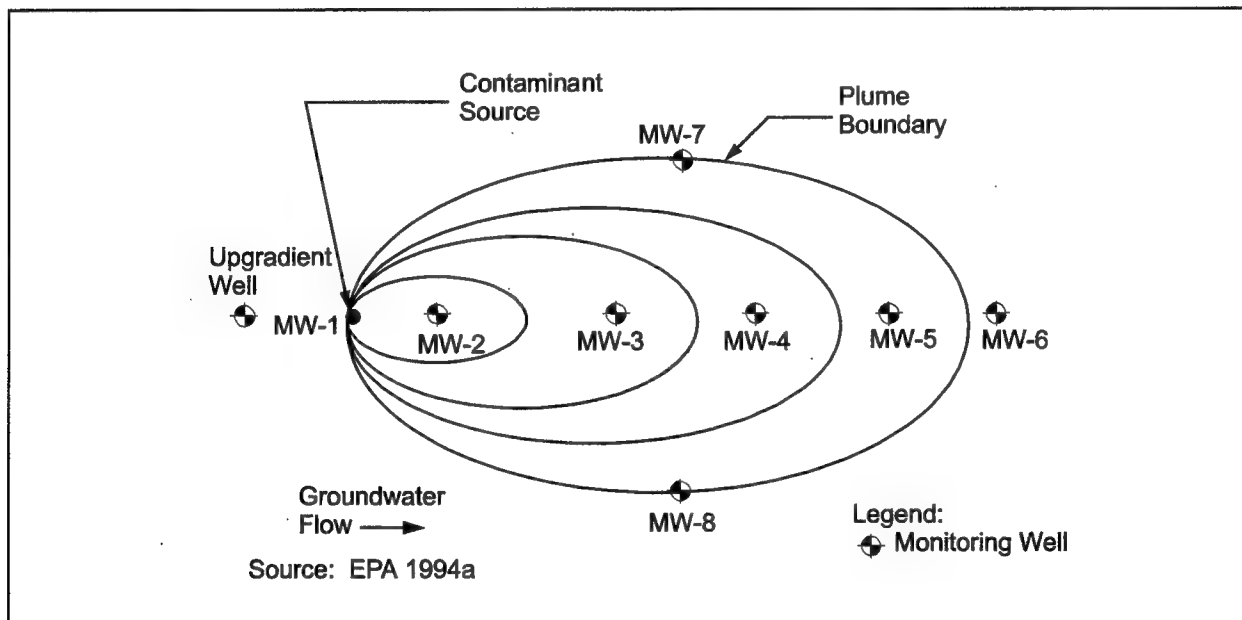


Figure 12. Idealized groundwater monitoring well network for monitoring natural attenuation

Requirements for soil sampling will depend upon specific site conditions such as volume, concentration, and distribution of contamination and upon the lines of evidence requiring verification. A typical soil sampling program may include sampling conducted over time at a specified frequency (e.g., annually) in areas of known contamination, as well as the boundaries of contaminated areas, to evaluate whether contamination is increasing or decreasing.

Explosives distribution in soils is typically extremely heterogeneous (Jenkins et al. 1997, 1998). Therefore, development of a sampling plan based upon distinct, achievable objectives and designed to effectively overcome the limitations imposed by extreme variability is imperative.

**Long-term protectiveness.** The implementation plan should provide for the identification and analysis of site-specific factors that, if changed over time, may

influence the long-term effectiveness of natural attenuation. These factors include, at a minimum, the following (flowchart references given in parentheses, Figure 11, Sheet 5):

- Potential changes in site characteristics or status that may affect the mechanisms of natural attenuation (e.g., chemical spills, changes in vegetation, construction activities, placement of land covers) (characteristics that may affect attenuation).
- Changes in hydrogeological characteristics due to new well development and other demands on ground water (hydrogeology).
- Changes in plans for the use of the site (use).
- Potential for new human and/or ecological receptors (human and/or ecological receptions).

**Evaluation of data.** Each time data are accumulated or after several sampling events, current contaminant mass and rate of reduction should be compared with predictions. The numerical model should be refined to reflect the new data and new predictions generated. If contaminant mass has not followed the predicted reduction rate, predictions must be adjusted and protectiveness reassessed.

**Development of contingencies.** The implementation plan should include the identification of appropriate contingencies to be implemented in the event that monitored natural attenuation is no longer adequately protective. Appropriate contingency alternatives are a natural product of the remedy selection process and may include engineering controls or the implementation of engineered remedial measures.

The need to implement contingencies may be identified through the results of monitoring activities or changes in factors that will affect the ability of monitored natural attenuation to be adequately protective. Examples of changes that may trigger the implementation of one or more contingencies include the following (EPA 1999; flowchart references given in parentheses, Figure 11, Sheet 5):

- Contaminant concentrations in soil or groundwater at specified locations exhibit an unanticipated increasing trend (increase in contaminant concentration).
- Near-source wells exhibit large concentration increases indicative of a new or renewed release (new or renewed release of contaminants).
- Contaminants are identified in sentry/sentinel wells located outside of the original plume boundary, indicating renewed contaminant migration (renewed contaminant migration).
- Contaminant concentrations are not decreasing at a sufficiently rapid rate to meet the remediation objectives (attenuation rate less than anticipated).
- Changes in land and/or groundwater use will adversely affect the protectiveness of the monitored natural attenuation remedy (change in site use).

Site-specific “triggers” must be defined in the contingency plan to clearly indicate when the contingency plan will be put into action. These triggers may

include any or all of the technical or the current and future use factors listed above.

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# Appendix A

## Microbial Degradation Potential

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Procedures for tracking microbial degradation processes for explosives in groundwater are limited to (a) monitoring concentrations of parent compounds and several transformation products and (b) monitoring subsurface conditions that are suitable for microbial activity in general, e.g., soil texture, organic carbon content, and nutrients. Until better tools are available, evaluation of the *potential* for microbial degradation can contribute to the weight of evidence for monitored natural attenuation as a remedial alternative. The laboratory tests described in this appendix provide evidence of degradation potential using soil taken from the aquifer. These samples are typically secured by cone penetrometry. The mineralization radioassays demonstrate the presence or absence of explosives mineralization activity and provide a potential mineralization rate. This is a measure of the potential of the actual site microorganisms to degrade TNT or RDX to carbon dioxide.

Results of these tests are not necessarily representative of degradation or degradation rates actually occurring in the aquifer. These tests represent the current best available technique for estimating degradation potential in the aquifer. Therefore, results can contribute to a weight of evidence for monitored natural attenuation as a remedial solution. Results will generally overestimate process rates because laboratory conditions have been optimized for the microbial processes. Conduct of tests at ambient (room) temperature is recommended for convenience and to improve generation of data above detection limits. However, any use of the data should be tempered with a conservative interpretation. For example, microbial degradation rates decrease by roughly 50 percent for every 10 °C drop in temperature, all other conditions remaining optimal. When natural heterogeneities in the distribution of microbes and contaminants and other natural variables are superimposed on "optimal condition," estimated rates and extent of degradation may be further reduced.

**Soil Mineralization Radioassays.** Soil mineralization radioassays for TNT and RDX are conducted according to the following procedure using soil from the site(s) of interest:

1. Following screening of soil samples (to less than 2 mm), homogenization, and mixing, 1.0 g subsamples are placed into triplicate, numbered, predried, and pretared aluminum weighing dishes and dried overnight at 105 °C to determine percent moisture. Dried samples are allowed to come to room temperature in a desiccator and then reweighed. The percent moisture content is determined by dividing the dried weight by the initial moist weight. An aliquot of the moist sample is set aside for nucleic acid and lipid biomarker analyses, if these are being done.
2. A set of twelve 250-mL biometers (Bellco Glass, Inc., Vineland, NJ) are cleaned for each soil by washing thoroughly, rinsing with concentrated hydrochloric acid followed by distilled water to remove the acid. Each biometer is further cleaned in a steam-cleaning dishwasher and autoclaved prior to use. Two milliliters of acetone is added to each unit, swirled, and allowed to sit for 5 min. A 1.0-mL sample of acetone is taken from each biometer and counted by liquid scintillation. This is done to ensure that all traces of radioactivity from previous studies have been removed. Flasks being used for the first time need only be washed in a steam-cleaning dishwasher and autoclaved prior to use.
3. A 30-percent soil slurry is prepared in nine cleaned biometers by adding 9 g of sieved, homogenized soil and 21 mL of sterile reverse osmosis or double distilled water to yield a total effective volume of 30 mL. Three additional biometers are autoclaved twice at 121 °C for 15 min.
4. The 12 biometer flasks are divided into the following three subsets:
  - (a) Nonsterile TNT mineralization (three replicates) and sterile untreated control (one replicate). Tests receive 0.2  $\mu$ Ci of U-[<sup>14</sup>C]-labeled TNT in unautoclaved soil. The sterile untreated control receives no TNT.
  - (b) Nonsterile RDX mineralization (three replicates) and sterile untreated control (one replicate). (Tests receive 0.2  $\mu$ Ci of U-[<sup>14</sup>C]-labeled RDX in unautoclaved soil. The sterile untreated control receives no RDX.
  - (c) Nonsterile acetate mineralization (three replicates) and sterile untreated controls (one replicate). Tests receive 0.2  $\mu$ Ci of <sup>14</sup>C-labeled sodium acetate in unautoclaved soil. The sterile untreated control receives no acetate.

Identical quantities of radiolabeled spikes are pipetted into triplicate scintillation vials and counted; the counts are used as time 0 values for radioactive materials added to the flasks.

5. Each test is swirled for approximately 5 min before adding 2.0 mL of fresh 1N KOH to the sidearm and sealing flasks with sterilized stoppers.



The tests are incubated on a gyratory shaker (100 RPM) at room temperature until assayed.

6. After 1, 5, 24, 48, 72, 96, and 120 hr of incubation, 2.0 mL of the KOH is removed from the sidearm of acetate tests. The sidearm is recharged with 2.0 mL of fresh KOH and resealed. A 1.0-mL aliquot of KOH is counted by liquid scintillation.
7. At intervals of 0, 10, 20, and 30 days, 1.0 mL of KOH from TNT, RDX, and control tests are assayed in the same manner as described for acetate. (Note: Total incubation time for acetate is shorter than for TNT and RDX because degradation of acetate is much faster.) The nonradioactive controls serve as the background count.
8. After assaying the 30-day TNT and RDX tests and the 5-day acetate tests, approximately five drops of concentrated  $\text{H}_3\text{PO}_4$  are added to the main well of each flask. The flask is resealed and returned to the shaker for 24 hr at room temperature. The following day, 1.0 mL of the KOH in the sidearm is assayed. A 1.0-mL sample is taken from the main well of each flask while continuing to shake. The sample is centrifuged at 676 relative centrifugal force (RCF) for 20 min, and the radioactivity in the liquid phase is determined by liquid scintillation counting. The solid phase remaining as a pellet from the centrifugation is dried to constant weight at 105 °C, combusted, and the  $^{14}\text{CO}_2$  produced is quantified by liquid scintillation counting. If a combustion method is unavailable, the radioactivity in the pellet can be estimated by difference.
9. Following completion of the radioassays,  $^{14}\text{CO}_2$  counts from KOH assays of each of the replicates on the same soil with the same isotope are summed to determine the cumulative  $^{14}\text{CO}_2$  released over the course of the incubation. The replicate cumulative values, corrected for the impurity of the radioisotope (purity is specified by the vendor, or can be measured), divided by the amount originally added to the test, represent the percent mineralization. This value divided by the incubation period (5 days for acetate, 30 days for radiolabeled TNT or RDX) gives an approximate rate of  $^{14}\text{CO}_2$  produced per day.
10. Replicate values of radioactivity for the solid phase for each soil with the same isotope are averaged together after correction for total volume of material in each biometer flask. This procedure is also conducted on the values for the liquid phases. The average values for liquid and solid phases are summed with the total cumulative  $^{14}\text{CO}_2$  values to yield mass balances for each soil-isotope combination. Acetate values obtained from soils having vigorous microbial populations are expected to have total mineralization values of 20 to 60 percent. TNT and RDX values are not considered significant until the total cumulative level  $^{14}\text{CO}_2$  reaches twice the impurity level of the radioisotope. For example, if the TNT is 97-percent pure, the impurity level would be 3 percent, and the

$^{14}\text{CO}_2$  production would need to be 6 percent before mineralization is considered significant.

Further details on this procedure can be obtained from Dr. Douglas Gunnison, U.S. Army Engineer Research and Development Center Environmental Laboratory, ATTN: CEERD-ES-P, 3909 Halls Ferry Road, Vicksburg, MS 39180-6199, 601-634-3873, FAX 601-634-4071, or e-mail [gunnisd@wes.army.mil](mailto:gunnisd@wes.army.mil).

# **Appendix B**

## **Louisiana Army Ammunition Plant**

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### **Physiography**

The Louisiana Army Ammunition Plant (LAAP) lies within the Western Gulf Coastal Plain physiographic province. Two major landforms, dissected uplands and rolling prairie, are found within LAAP. Minor landforms include abandoned channels, typically filled with clays, which were deposited by ancient courses of the ancestral Red River. Relief at LAAP is moderate with elevations varying from about 39.6 m (130 ft) mean sea level (MSL) near Dorcheat Bayou to 24.4 m (80 ft) MSL at Clarke Bayou.

### **Regional Geology**

Regionally, LAAP lies within the North Louisiana Syncline. This syncline, a subsurface structural feature, lies on the eastern limb of the Sabine Uplift and was formed by deformation of sediments during tectonic activity, which began approximately 225 million years ago (Paleozoic Era). The LAAP region is bounded to the east by the Monroe Uplift and to the west and north by the Sabine Uplift. Smaller local uplifts exist in the area and significantly modify the local structural geology (i.e., formation dip) and groundwater flow regime in the vicinity.

The shallow deposits at LAAP consist of unconsolidated Pleistocene age silts (ML), silty sands (SM), fine sands (SP-SM), and clays (CL-CH) according to the Unified Soil Classification System (U.S. Army Engineer Waterways Experiment Station 1960; Howard 1977). The sediments occur as fining upwards sequences of materials which were deposited as fluvial terraces associated with the ancestral Red River. Maximum thickness of these deposits is about 18.3 m (60 ft), but local variations are present. Immediately underlying the terrace deposits is the Cane River Formation. This unit consists of overconsolidated claystones and is not an aquifer in this area.

## Site Function and Evolution

LAAP is a government-owned contractor-operated facility located 35.4 km (22 miles) east of Shreveport, LA. The primary mission of the 6,062-ha (14,974-acre) plant was to load, assemble, and package ammunition items, manufacture ammunition metal parts, and provide associated support functions for ammunition production. Eight ammunition lines and one ammunition nitrate graining plant were constructed by the Silas Mason Company between July 1941 and May 1942. Production ceased in August 1945 at the conclusion of World War II. The plant was then placed on standby status in September 1945, and in November of 1945 the Federal Government relieved Silas Mason Company of responsibilities for the plant operations.

In February 1951 with the outbreak of the Korean Conflict, Remington Rand Corporation reactivated LAAP under contractual agreement with the Federal Government. Ammunition production was suspended in October 1957, and again the facility was placed on standby status. The Federal Government again reactivated the facility in September 1962 and contracted with Sperry Rand Corporation to operate munitions production in support of the Vietnam Conflict. In 1974 Thiokol Corporation took over the facility operations when Sperry Rand Corporation relinquished its contract. Thiokol Corporation maintained the facility until the summer of 1996 when most operations at the plant ceased. As of August 1997, five contractors were bidding to resume very limited production of black powder products at a single load line (Y line).

## Historical Contaminant Data

LAAP was placed on the National Priorities List in March 1989 due to contamination caused by past disposal of explosives-laden wastewater in 16 unlined surface impoundments located in Area P (Figures B1 and B2). An interim remedial action was initiated in 1988 because investigations indicated that the lagoons were a source of contamination and were contributing explosives to the groundwater system. The lagoons were remediated by draining and treating wastewater and incinerating soils. The lagoons were excavated until a total field-determined explosive concentration of less than 100 parts per million was reached. The incineration of 101,929 tons of soil and the treatment of 53,604,490 gal of wastewater and rainwater collected within the 16 lagoons was completed in 1990. The area was then backfilled with the incinerated soil, capped, and vegetated. The lagoons were covered with a minimum 0.6-m-(2-ft)-thick compacted cap of uncontaminated clay soil from Area P and a nearby borrow pit located north of the lagoons. This clay cap covers all of the original Area P including the former lagoons and is compacted to at least 90 percent of

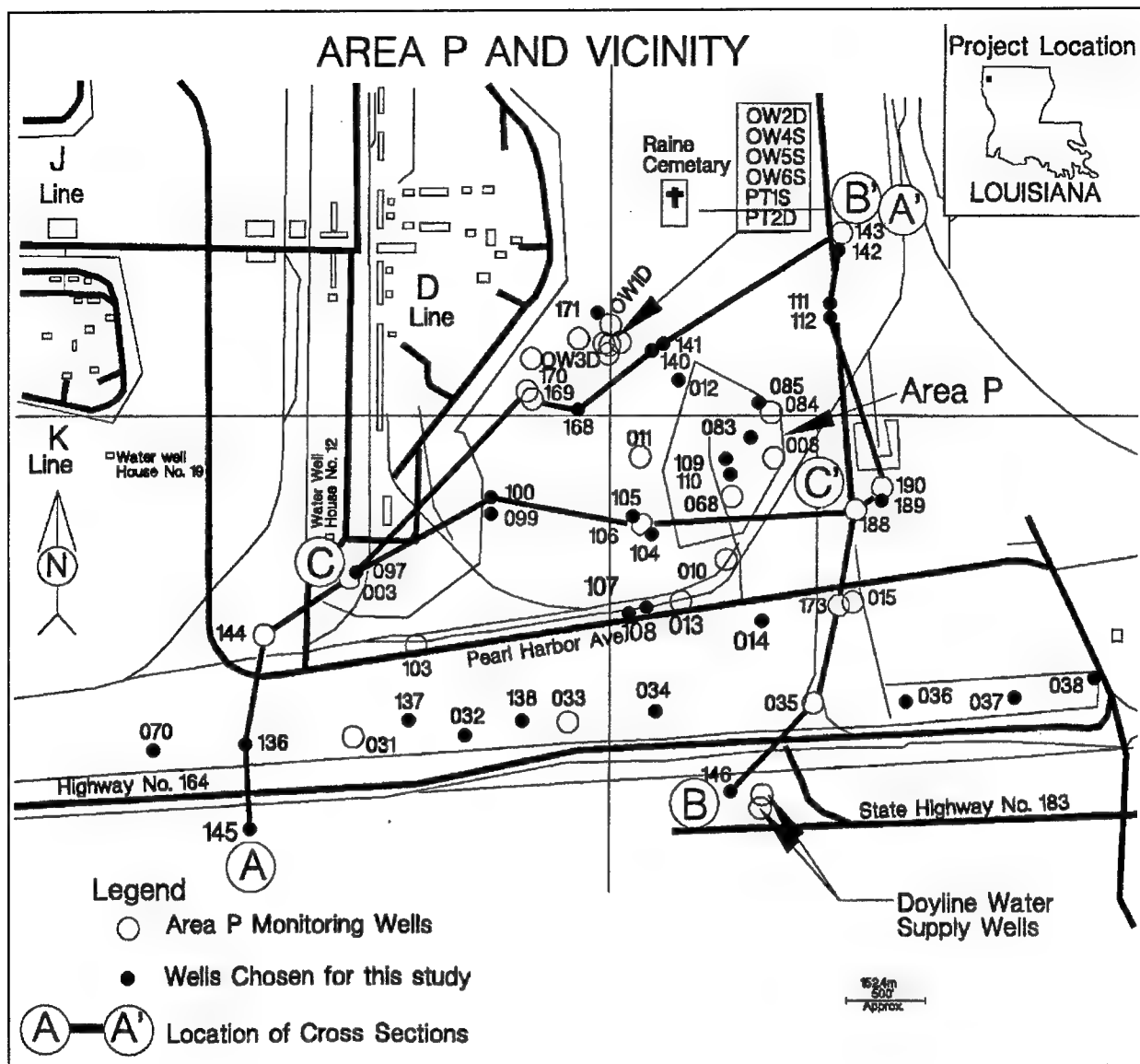


Figure B1. Louisiana Army Ammunition Plant - Area P and vicinity

the standard proctor density for the clay used. The cap is covered with 10 cm (4 in.) of topsoil and has a slope of at least 1 percent to facilitate drainage.

In 1989 Science Applications International Corporation (SAIC) under contract to the Army Environmental Center (USAEC) began a 5-year review to assess the effectiveness of the interim remedial action at Area P. The review was conducted in accordance with the Comprehensive Environmental Response, Compensation, and Liability Act of 1980. The final report was submitted to USAEC in August of 1994 (SAIC 1994). In this final report, a statistical regression analysis approach was used to identify the groundwater trends at Area P. Groundwater sampling data from 1980 through 1994 were evaluated. Quadratic and linear analyses were conducted for 108 sampling data sets. Trend categories were assigned to each of the data sets based on improving

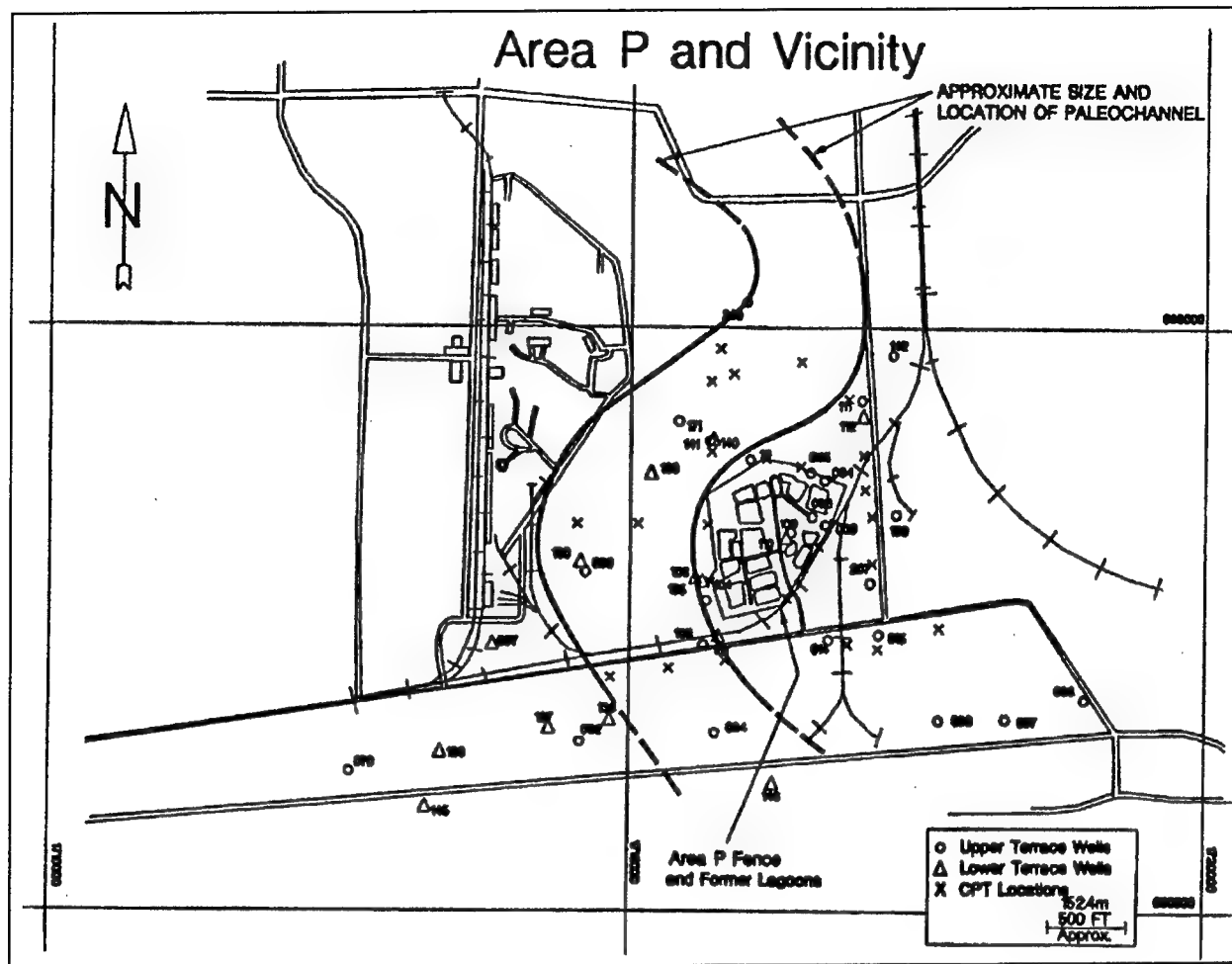


Figure B2. Location of former Area P lagoons

deteriorating and stable groundwater quality with regards to explosives. In these data sets, no specific trends were identified, but in general, the overall quality of water in the Upper and Lower Terrace aquifers at Area P was improving (SAIC 1994).

## Historical Geological Data

Historical geological reports (Louisiana Department of Conservation 1954; Snider 1983; U.S. Army Corps of Engineers (USACE) 1984 and 1987; Engineering Technologies Associates (ETA) 1991; SAIC 1994; International Technology Corporation 1997) and cone penetrometer data gathered for the natural attenuation demonstration project (Pennington et al., in preparation) indicated that the shallow aquifers underlying LAAP consist of Pleistocene age terrace deposits unconformably overlying the Cane River Formation (Figures B3, B4, and B5). The Terrace deposits in Area P are subdivided into the Lower Terrace consisting of fine sands and a trace of gravels and the Upper Terrace

# AREA P - LAAP

## Section A-A'

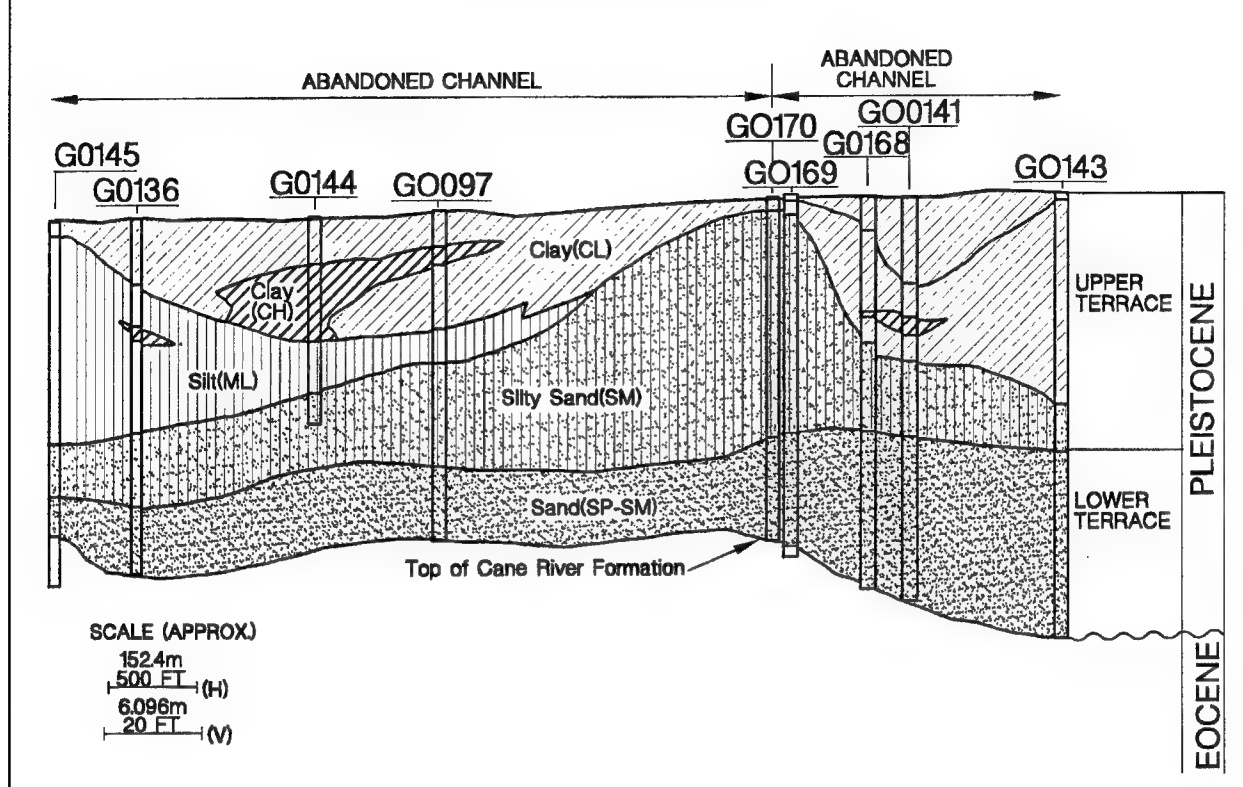


Figure B3. Area P geologic Cross Section A-A'

consisting of very fine grained silts, clays, and silty clays. An intermediate clay unit is present at some locations, is not uniform over the entire site, and is totally absent at many locations. However, the unit does serve as a limited aquitard as evidenced by the Paleochannel defined by the cone penetrometer (Figure B2). Collectively, these Pleistocene age units are a fining upwards sequence. The Eocene age, Cane River Formation consists primarily of clay or clay sufficiently indurated to be classified as a claystone. The Cane River Formation is not an aquifer beneath Area P, and is, therefore, considered the confining layer for modeling the site.

Groundwater in the Upper Terrace aquifer generally exists under water table (unconfined) conditions at depths varying from approximately 1.5 to 7.6 m (5 to 25 ft) below sea level (BSL). The Lower Terrace aquifer, while not present in all areas, typically occurs from 7.6 m (25 ft) BSL to the top of the Cane River, which is about 15.2 m (50 ft) BSL. The Lower Terrace aquifer also tends to produce more water than the Upper Terrace deposits. Although none of the Terrace deposits supply water to production wells on the installation, some domestic wells in Houghton, Princeton, Dixie Inn, Minden, Sibley, and Doyline

## AREA P - LAAP Section B-B'

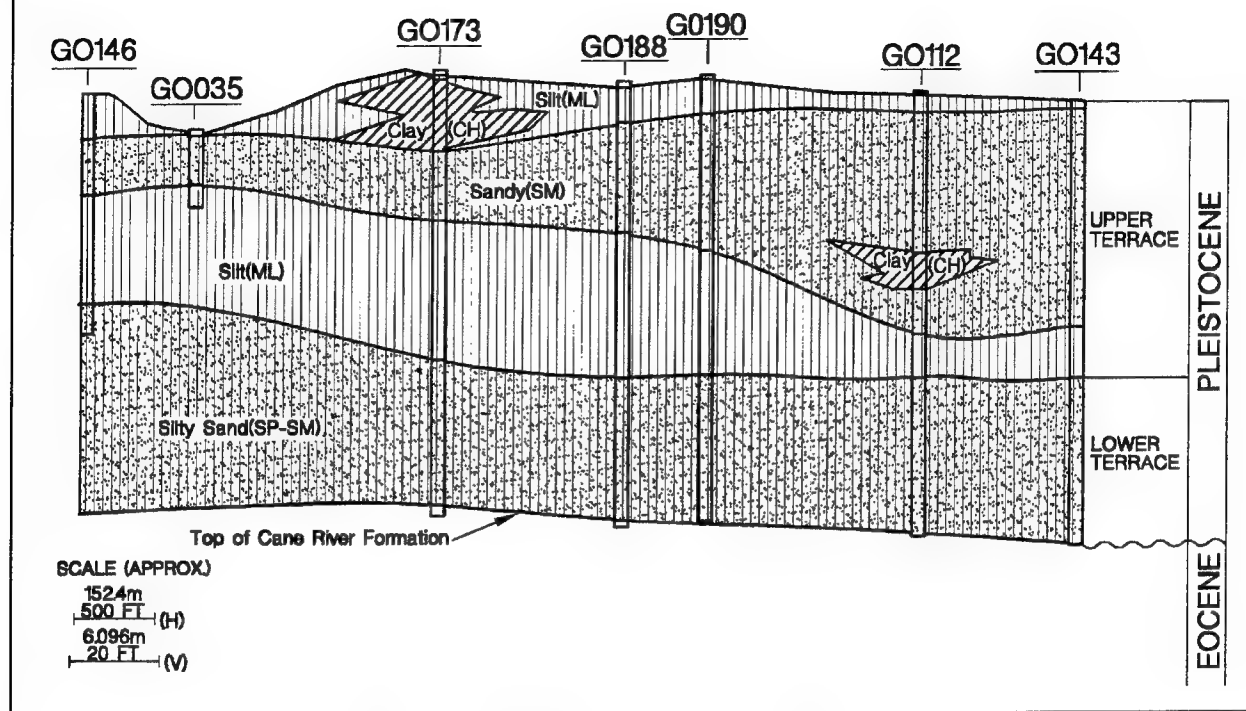


Figure B4. Area P geologic Cross Section B-B'

are completed in the Terrace deposits. Groundwater quality modeling conducted for Area P indicated that contaminant (explosives) migration in the Upper Terrace generally traveled downwards with little horizontal spreading (ETA 1991). Further, the modeling and water level measurements indicated that the regional groundwater flow in the Upper Terrace aquifer was southwest. Water level data collected for the natural attenuation demonstration project (Pennington et al., in preparation) indicated that groundwater movement is in different directions in the Upper versus the Lower Terrace aquifers. The rate and direction of groundwater movement are also influenced by the Paleochannel located on the western edge of Area P.

### Cone Penetrometer Sampling Event

A cone penetrometer (CPT) and hydropunch (HPT) sampling event was conducted to support the natural attenuation demonstration between



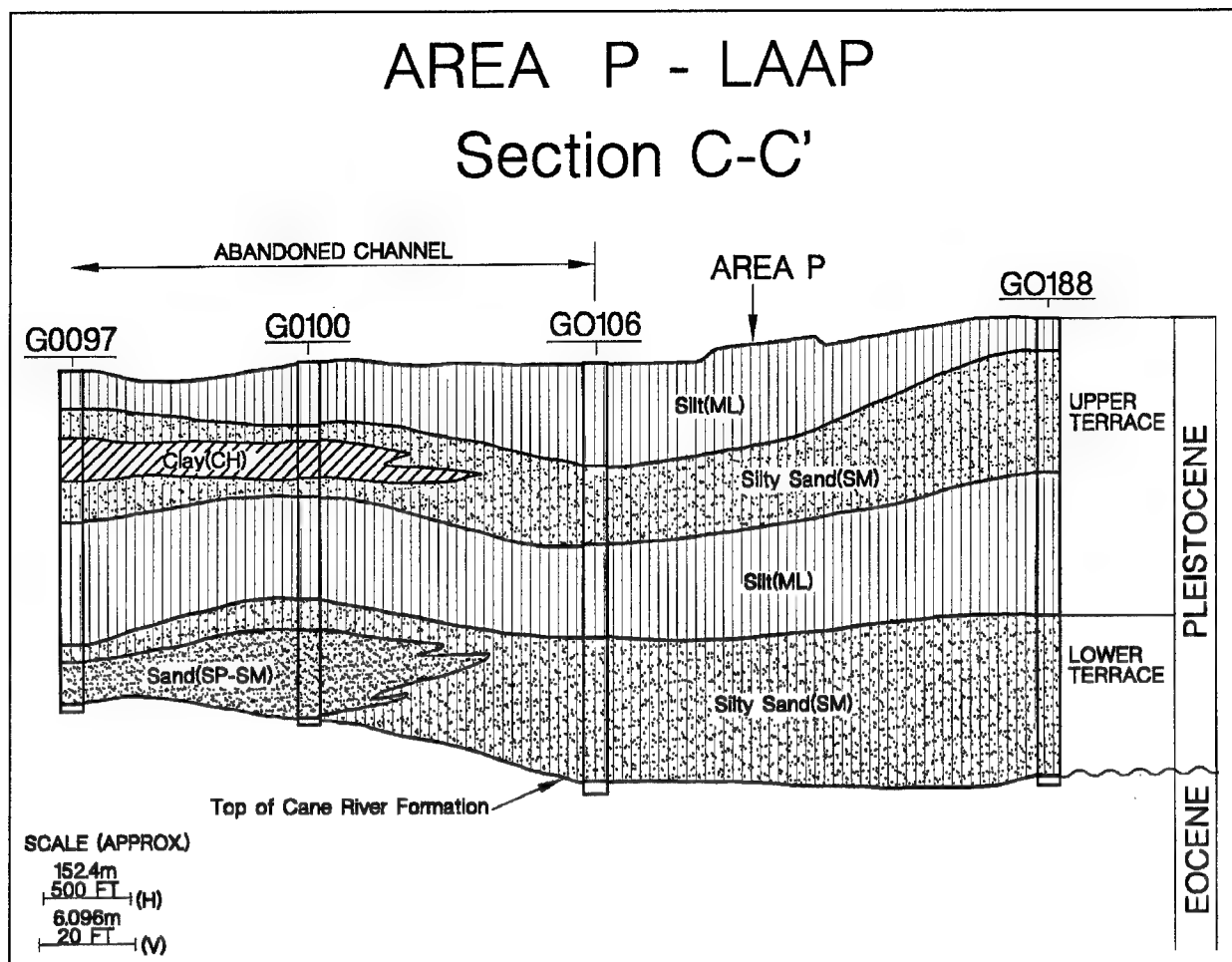


Figure B5. Area P geologic Cross Section C-C'

September 9 and 29, 1996 (Figure B2). Soil samples were collected from 24 locations along 8 transects. Penetrations were through the entire Upper and Lower Terrace sections. Generally, the penetrations were about 15.2 m (50 ft) deep and reached total depth in the Cane River Formation. The locations were selected on the basis of groundwater sampling data collected monthly during the previous 6 months. Additional data collected at the site (USACE 1984) was utilized to stratify the various lithologies at Area P and assist in the location of the sampling sites for the 1996 events. TNT and RDX concentrations from previous groundwater sampling were contoured to identify "hot spots" and potential source areas. Transects were located to ensure sampling along a line extending from the zone of highest concentrations to a zone of zero concentration in all four cardinal directions from the source (original lagoons). A thin vertical slice of the soil obtained in the split spoon was removed and analyzed in the field for explosives (Jenkins 1990). The remainder of the sample was retained for laboratory confirmation of explosives and additional research. Vertical profiles of soil were collected at five locations. The number of depth intervals sampled depended upon the depth of the CPT hole at each location.

These soil samples were used to measure vertical variations in permeability for the groundwater model and for other research.

Analysis of existing geological information indicated the existence of a Pleistocene-aged paleochannel on the western edge of Area P (Figure B2). This paleochannel was first observed as a meander scar (abandoned channel), visible in some of the earliest aerial photographs of the site. The dimensions of the paleochannel were defined by the CPT sampling in 1996. The paleochannel is at least 61 m (200 ft) wide (122 m (400 ft) at some locations), and 7.6 to 9 m (25 to 30 ft) deep. The hydrogeologic effect of this feature is that the low permeability clays and silty clays in the paleochannel act as an aquitard which locally separates the Upper and Lower Terrace aquifers, steering the contaminants to the Lower Terrace, which in this area has a higher permeability.

## **LAAP Groundwater Monitoring Plan**

*Well Selection Procedures:* Time series data plots from 61 wells in the Area P vicinity were reviewed for the natural attenuation demonstration project to determine any trends of declining concentrations for TNT, RDX, and the TNT daughter products, TNB, 2,4-DNT, and 2,6-DNT. This data set was obtained from a previous remedial investigation and feasibility study conducted at LAAP in the 1970s and 1980s (Dames and Moore 1993). The objective was to select representative wells from both the Upper and Lower Terraces. Selection criteria included spatial distribution of wells relative to the original source, the conceptualization of the contaminant plume, location of potential receptors, and the completeness of historical data. Other selection criteria included reliable well completion data on the kind of well screen type and well depth and performance data such as yields.

*Well Sampling Procedures:* Thirty wells were selected and sampled by micropurge (low-flow) techniques (Gass et al. 1991; Garske and Schock 1986; Puls, Eychaner and Powell 1990; and Puls et al. 1991 and 1992). A 5-cm- (2-in.-) diam low-flow pump was utilized for sampling wells having a diameter as small as 10 cm (4 in.). Field parameters were measured with an in-line continuously monitoring unit with data transmitted directly to a laptop computer. Ecowatch software (Yellow Springs Instruments, Yellow Springs, MO) was used to visualize in real-time the parameters being measured. These parameters included pH, conductivity, dissolved oxygen (DO), temperature, and salinity. Formation water may be obtained by three options: (a) micropurge using a low-flow pump until a stable DO value is obtained, (b) bailing a minimum of three well volumes, or (c) micropurge and bailing in combination.

To obtain formation water at LAAP, a micropurge technique was used by which discharge was matched to recharge. The original sampling procedures called for three successive DO readings within 10 percent of each other. Due to low-permeability materials at LAAP, stable DO proved difficult to achieve and was, therefore, abandoned in favor of purging three well volumes.

## Use of the Cone Penetrometer and Hydropunch

CPT/HPT is a cost-effective means of providing real-time groundwater contamination data. Important additional data that can be obtained simultaneously are stratigraphy and resistivity. Resistivity can be directly related to subsurface soil/aquifer material characteristics such as particle-size distribution. These data are especially relevant for modeling of the site. Other major advantages of the CPT/HPT include elimination of the placement of unnecessary monitoring wells, groundwater sampling from multiple aquifers, a self-contained decontamination system, and a mechanism for repeated sampling at a given location. Because the CPT/HPT uses no drilling fluids (drilling mud) and pushes into the soil rather than drilling, no drill cuttings (soils) or drilling mud is generated. Collection of CPT samples along transects and within vertical profiles can define the lateral and vertical extent of the contaminant plume(s). Soil samples up to approximately 300 g are routinely recovered with the split spoon sampler. The samples furnished lithological data for the numerical modeling and samples for additional research. The HPT punches a 0.9-m (3-ft) well screen, 3.8 cm (1.5 in.) in diameter to the desired depth. The amount of water obtained is dependent upon the permeability (recharge) of the formation and its depth. Typically, volumes of up to several gallons can be obtained from the more permeable lithologies such as sands (SP) and silty sands (SP-SM).

Disadvantages of CPT sampling are the great size and weight of the truck (i.e., 22,680 kg (50,000 lb)), which can create handling and maneuvering problems in soft or muddy soils. A limitation of the current sampling tools is that only unconsolidated materials can be sampled.

Existing site data can be used for more efficient placement of CPT sampling points and monitoring wells. CPT transects (oriented in all four directions) may be sufficient if a reasonable amount of geologic and analytical data exists. If only a small amount of data is available, CPT transects oriented radially from a "hot spot" or known source is advisable. Sample spacing is also dependent upon the available data, but typically can be several hundred feet or much more if sufficient data exist. At LAAP, the initial spacing was about 183 m (600 ft), with additional penetrations as needed. Once the plume is defined in all four directions, profile samples can be collected at strategic sites. These data coupled with the line or transect samples can effectively define the horizontal and vertical extent of the explosive plume.

## Hydrogeology

Groundwater levels at LAAP were highest in late winter and lowest in the fall, which is typical. Seasonal variations were slight, since low permeability precludes rapid movement or recharge. The direction of groundwater movement is to the southwest in the lower terrace and to the east possibly towards Dorcheat Bayou in the upper terrace.

## Trends in Historical Site Data

The extreme variability of the historic contaminant concentration data for wells in Area P made determinations of trends in concentration over time difficult. Observed concentrations of some explosives span several orders of magnitude in the most highly contaminated area in both the upper and lower terraces. Analyses of the data may be summarized as follows:

- a.* No significant trends over time for RDX, tetryl, and 2,6-DNT.
- b.* TNT, TNB, DNB, 2,4-DNT, and HMX increasing over time in the most highly contaminated area of the lower terrace aquifer.
- c.* TNT, TNB, and HMX decreasing over time in the less contaminated outer zone of the lower terrace aquifer.
- d.* Fewer trends in the upper terrace than in the lower terrace aquifer.
- e.* All explosives below detection limit in all water supply wells.

Most of the historical data were collected prior to source removal. Therefore, the implications of historical data trends for future contaminant trends are limited. A detailed description of the historical data and the statistical processing of the data are given in the Interim Report (Pennington et al. 1999).

## Results of Groundwater Monitoring

Trends in contaminant concentrations over the 2-year study period were analyzed statistically for the 11 wells in which most analytes were consistently detected. Significant declines in contaminant concentrations occurred in 9 of the 11 wells (Figure B6). Contaminant mass calculations also indicated declining mass from 51.97 and 77.74 to 49.87 and 68.04 metric tons for TNT and RDX, respectively.

## Results of Site Capacity Estimates

Aquifer soils from LAAP were generally high in sand, ranging from 65 to 92.5 percent sand. Silt and clay were present in all samples, although in lower amounts. Total organic carbon content was low, ranging from 0.015 to 0.162 percent. Cation exchange capacity (CEC) was also low, ranging from 3.5 to 8.1 Meq 100 g<sup>-1</sup>. Soil pH was acidic and relatively consistent for all soil types (average of 5.55). Permeabilities of the soils ranged from 10<sup>-4</sup> to >10<sup>-9</sup> cm sec<sup>-1</sup>.

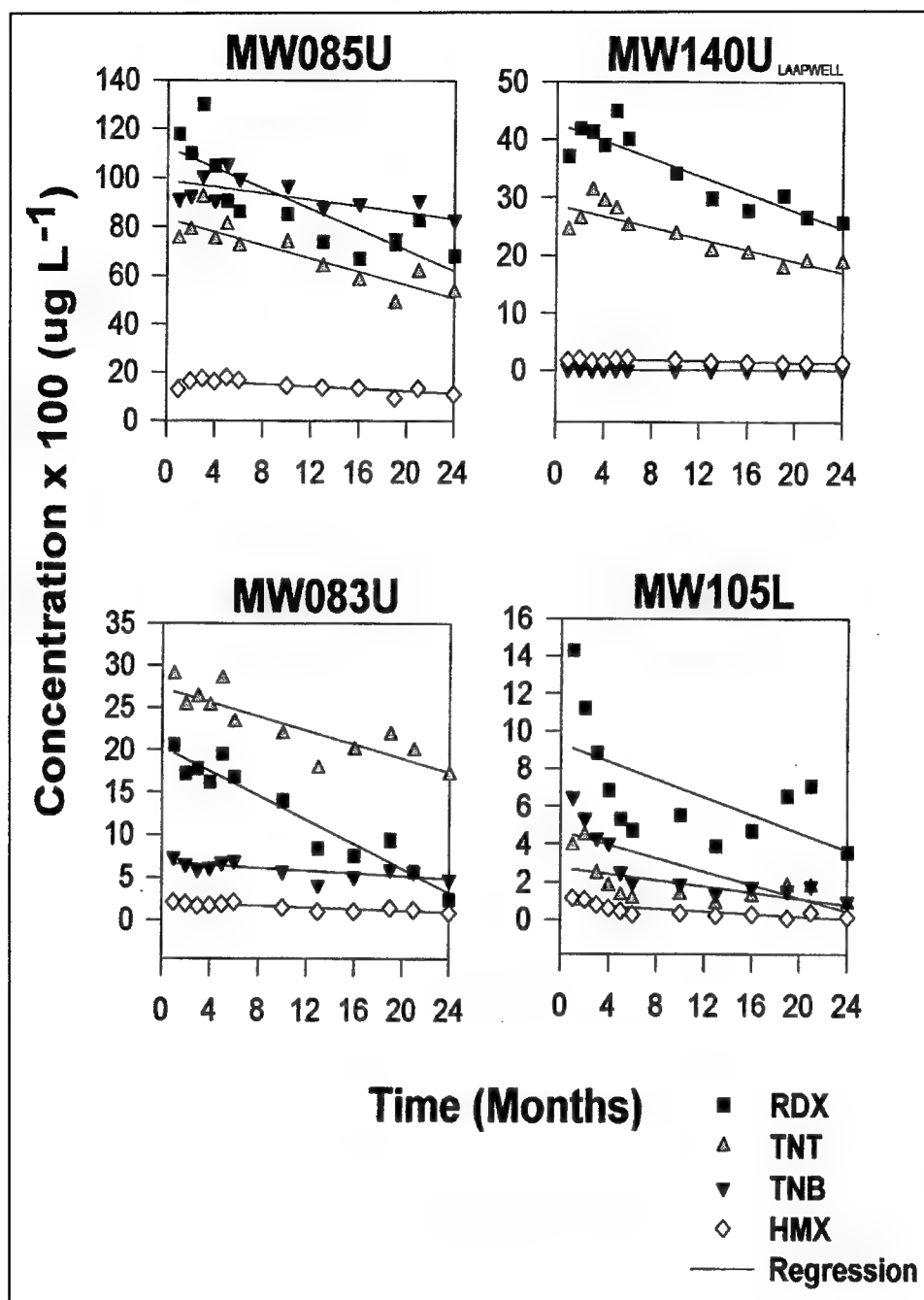


Figure B6. Trends in explosives concentrations in selected monitoring wells over the 2-year sampling period at LAAP

Adsorption of explosives from groundwater by the LAAP aquifer soils was limited. The measured values of  $K_d$  were below  $1 \text{ L kg}^{-1}$  for all soils and contaminants, ranging from no significant adsorption to a high value of  $0.84 \text{ L kg}^{-1}$ . The highest degree of sorption was associated with the soils highest in clay and CEC. The range of sorption coefficients between soils varied over an order of magnitude for explosive compounds. For modeling of contaminant

transport at the LAAP site, the use of an average value of  $K_d$  to represent sorption at the site was appropriate. Although these data indicate limited retardation, low permeability may exert a greater influence on movement of the plume than is exerted by sorption and transformation. These results suggest that mass transport limitations rather than site capacity restrict transport at LAAP.

## Biomarker Results

Rates of TNT and RDX mineralization were very low in LAAP soils. Rate constants for TNT ranged from less than  $1 \times 10^{-4}$  to  $2.2 \times 10^{-3}$ ; for RDX the range was from less than  $1 \times 10^{-4}$  to  $2.0 \times 10^{-3}$ . Few significant correlations between geochemical parameters and biomarkers were found. Several nucleic acid probes correlated positively with mineralization rate as did the following parameters determined by lipid biomarkers: biomass, abundance of gram-negative, sulfate-reducing and iron-reducing bacteria, and a sulfite reductase. The potential for aerobic degradation of TNT in LAAP soils was suggested by the presence of two catechol oxygenase gene probes. Other observed genes supported potential for both anaerobic and aerobic metabolism of TNT.

## Lessons Learned

Results of the groundwater monitoring at LAAP supported the first line of evidence required under EPA guidance for verification of monitored natural attenuation, i.e., declining contaminant mass. Lessons learned for effective monitoring include the following:

- a. Consistent implementation of good sampling practices is essential to achievement of quality data. To that end all parties involved in sampling, handling, and analysis should follow a consistent plan. Deviations from established protocols can greatly impact the observation of small trends over short observation periods.
- b. To ensure that highly contaminated well water cannot cross contaminate less contaminated water, sampling should progress from low to high concentration wells; sample tubing should be dedicated to each well; and all sampling apparatus that comes into contact with the groundwater should be decontaminated between wells. To ensure that the decontamination procedure is effective, random samples of rinsate from decontamination should be submitted for explosives analyses. At LAAP one such sample was analyzed for each sampling day.
- c. Oxygenation of the water in contact with air in the well before pumping caused a decrease in explosives concentrations. Therefore, removal of this oxygenated water, which can introduce an artifact into the explosives concentration data, is essential. Additional studies showed that explosives concentrations stabilized when DO reading stabilized as water was

pumped from the well using a micropurge technique. This technique was adopted for LAAP well sampling. However, micropurge techniques cannot be used under conditions of low well volume. Therefore, well volumes removed when explosives concentrations and DO stabilized were calculated. For LAAP, removal of three well volumes by bailing was roughly equivalent to stabilization of DO and explosives concentrations.

- d.* Experiments were conducted at LAAP to determine the best sample preservative for the explosives analytes (Pennington et al. Interim Report). Results indicated that acidification to pH 2 with 1.5 g sodium bisulfate per liter of groundwater was effective. Therefore, all groundwater samples for explosives analyses were so preserved.
- e.* At least 1 of every 10 samples should be collected and analyzed in duplicate to ensure precision in the data. At least two spiked blanks (distilled or reverse osmosis water) and three spiked groundwater samples should be analyzed for each sampling event to ensure accuracy. Spikes should represent both low and high analyte concentrations. Temporal representativeness of the data can be obtained by sampling with sufficient frequency to observe seasonal trends that may affect overall explosives concentration trends. At LAAP sampling was quarterly for 2 years. Spatial representativeness can be obtained by sampling from representative locations throughout the groundwater plume. At LAAP 30 aerially distributed wells were sampled, including wells at different depths.
- f.* Sampling efficiency was optimized by using two two-man field crews. While one crew monitored and demobilized at one well, the other crew set up and initiated monitoring at the next well. Using this "leap frog" technique greatly reduced well sampling time.

Site capacity (see Step 4 of this Protocol) and biomarker techniques (see Step 4 and Appendix A) contributed to a weight-of-evidence by estimating rates of attenuation. Numerical models predict significant continuing reductions in contaminant masses of TNT and RDX over 20 years (Appendix D). The slow transport at LAAP coupled with the demonstrated decline in contaminant mass and the potential for microbial degradation provide evidence of the viability of monitored natural attenuation as a remedial alternative for the site.

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# **Appendix C**

## **Model References and Sources**

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Computer Model	Information Provided	Comments	Model Distribution Address
<b>Screening Level Analytical Solutions Requiring Minimum Site Data</b>			
AT123D	Simple analytical model; simulates three-dimensional contaminant transport through the groundwater; requires flow data to run.	Simple, screening-level model; does not simulate flow distribution.	Scientific Software Group, P. O. Box 23041, Washington, DC 20026-6793. Phone: 703-620-9241
BIOSCREEN	Analytical solute transport model programmed in Microsoft Excel; simulates advection, dispersion, adsorption, and first-order decay.	Easy to use; fixed and simplified modeling domain, geometry, and contamination.	National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK 74821-1198. Phone: 405-436-8652
<b>Numerical Models Requiring Detailed Site Data</b>			
MODFLOW	Simulates time-varying groundwater flow in three dimensions.	Only calculates groundwater flow field in saturated zone; does not simulate chemical transport; included in GMS. <sup>1</sup>	USAE Waterways Experiment Station, 3909 Halls Ferry Road, Vicksburg, MS 39180.
MODPATH	Uses output from MODFLOW to determine contaminant transport paths.	Uses simple particle pathways; good for estimating potential exposure pathways; does not simulate contaminant concentrations; included in GMS. <sup>1</sup>	USAE Waterways Experiment Station, 3909 Halls Ferry Road, Vicksburg, MS 39180.
MT3D	Simulates spatial and temporal variation of contaminant concentrations over time; includes advection, dispersion, diffusion, sorption, and decay parameters.	Used in conjunction with model that simulates flow field (e.g., MODFLOW); calculates chemical concentrations in space and time; included in GMS. <sup>1</sup>	USAE Waterways Experiment Station, 3909 Halls Ferry Road, Vicksburg, MS 39180.
BIOMOD3-D	Simulates chemical transport and transformation in fractured and porous media; linked to MODFLOW; includes complex methods for evaluating microbial processes.	Must be used in conjunction with model that simulates groundwater flow field (e.g., MODFLOW).	Scientific Software Group, P. O. Box 23041, Washington, DC 20026-6793. Phone: 703-620-9241
RT3D	Three-dimensional, multispecies, and biologically reactive transport model based on MODFLOW and MT3D codes; kinetic modules either available or may be developed by the users.	Based on saturated flow model; has been applied to chlorinated solvent problems; can be modified for explosives; included in GMS. <sup>1</sup>	Battelle, Pacific Northwest National Laboratory (PNNL), P. O. Box 999, Richland, WA 99352. Phone: 509-373-0998
SESOIL	Simulates moisture and contaminant transport through the unsaturated zone.	Simulates transport in unsaturated zone only; may be used to estimate sources to groundwater contamination.	Oak Ridge National Laboratory, Computational Engineering Section, Oak Ridge, TN 37831-2008. Phone: 423-576-7556
FEMWATER	Simulates density-driven, coupled flow and contaminant transport in both the saturated and unsaturated zones.	Calculates flow and mass transport of one chemical in each simulation; supports first-order decay only; included in GMS. <sup>1</sup>	USAE Waterways Experiment Station, 3909 Halls Ferry Road, Vicksburg, MS 39180.
<sup>1</sup> The Department of Defense Groundwater Modeling System (GMS).			
<i>(Continued)</i>			

Computer Model	Information Provided	Comments	Model Distribution Address
3DFATMIC	Three-dimensional subsurface flow and transport of microbes and chemical model based on FEMWATER.	Coupled flow and transport model with biodegradation and microbial biomass production options; saturated-unsaturated media.	National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK 74821-1198. Phone: 405-436-8652.
UTCHEM	Simulates 3-D, multiphase flow, N-constituent reactive transport, finite difference model capable of simulating user-defined reaction pathway with variety reaction kinetics, microbial process.	A very detailed model; requires extensive site data; will be included in GMS. <sup>1</sup>	USAE Waterways Experiment Station, 3909 Halls Ferry Road, Vicksburg, MS 39180.
BioF&T	Simulates advection, dispersion, diffusion, adsorption, desorption; includes complex methods for evaluating microbial processes.	Useful for assessing complex methods of evaluating microbial processes.	Scientific Software Group, P. O. Box 23041, Washington, DC 20026-6793. Phone: 703-620-9241

# **Appendix D**

## **Groundwater Modeling at Louisiana Army Ammunition Plant**

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### **Introduction**

Numerical modeling can be used to integrate site hydrogeology and contaminant distribution with results from laboratory testing and biomarker investigations to predict the effectiveness of natural attenuation in regulating contaminant transformation and transport. The combined effect of advection, adsorption, and degradation on the persistence of explosives can be evaluated. At the Louisiana Army Ammunition Plant (LAAP) site, explosives may be sorbed by soil particles, immobilized by chemical interactions with soil components, and degraded by microorganisms. These processes may vary spatially. The transport of chemicals can occur by percolation of water and may be retarded or delayed compared with the fluid flow. Biochemical, chemical, and physical processes collectively act to modify contaminant concentration and distribution over time and space. Field measurements provide a snapshot of the site geochemistry and microbiology at a specific time. Chemical, physical, and biological data from a site can be integrated into a framework that supports natural attenuation of explosives using numerical models.

Numerical modeling was applied to the LAAP site using information derived from site monitoring, site capacity testing, and biomarker analyses. The objectives of the numerical modeling effort were as follows: (a) provide a three-dimensional (3-D) visualization of contaminant distribution at the site, (b) evaluate the dominant factors affecting natural attenuation at the site, and (c) predict long-term contaminant migration and transformation.

## Groundwater Modeling System (GMS)

The Department of Defense Groundwater Modeling System (GMS) (1996) version 2.0 is a comprehensive computer graphical system, which includes modeling tools to facilitate site characterization, model conceptualization, mesh and grid generation, geostatistical computations, and postprocessing. GMS is a state-of-the-art graphical computer interface that is linked with groundwater transport and water quality models to predict the fate and transport of contaminants at a site.

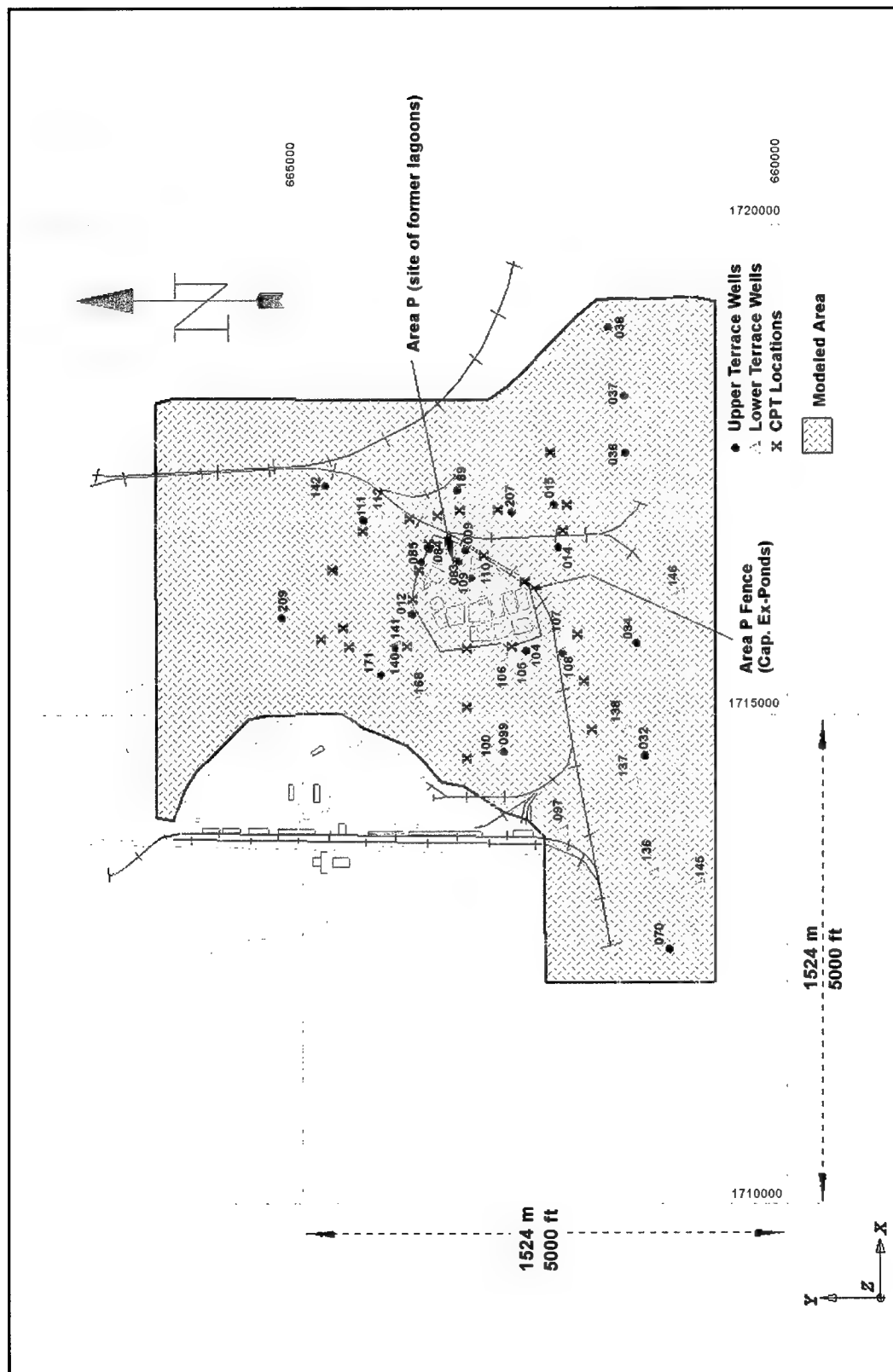
To visualize and model the distribution of explosives at the LAAP site, GMS with its subsurface flow and transport model, FEMWATER (Lin et al. 1997), was applied. Several geostatistical (interpolation/extrapolation) numerical tools are integrated into GMS for this purpose. In the 3-D space, these include inverse distance weighted, natural neighbor, and kriging. Each of these approaches has its own merits. The reader is referred to the GMS user's manual for detailed descriptions of these options.

## Conceptual Model

The first step in numerical modeling is to develop a conceptual model that describes essential components of natural phenomena and hydrogeological conditions in a simplified form. A conceptual model based on LAAP site geological and chemical data was developed that incorporates information from the site borehole geology, hydraulic conductivity, and flow boundary conditions.

Hydraulic conductivity, porosity, recharge rates, and contaminant concentrations vary spatially over the site. Full characterization of the heterogeneity of the aquifer is not possible due to limitations in hydraulic conductivity measurements and associated errors and uncertainties. In addition, definitive information about boundary conditions and recharge rates is usually unavailable because of the complexity of the geology of the aquifer and lack of reliable means to measure or estimate fluxes at boundaries, or recharge rates and their distribution. For this site, discrete hydraulic conductivity data were interpolated/extrapolated to estimate properties at intermediate points of the numerical mesh. A combination of GMS geostatistical tools was used to develop a numerical representation of the site.

The modeling domain at the ground surface of the LAAP site included the former lagoon area and proximal monitoring wells (Figure D1). Four stratigraphic units were identified at LAAP based on lithologic data. The units were a vadose zone (unsaturated soil), an upper terrace aquifer, a semiconfined layer, and a lower terrace aquifer. The vadose zone and the upper terrace aquifer form a shallow unconfined aquifer. The terrace deposits are composed of alternating beds of mixed sands and clay. The values of hydraulic conductivity for each layer and node of the 3-D modeling mesh (Figure D2) were estimated from the data given in Table D1 using GMS geostatistical tools.



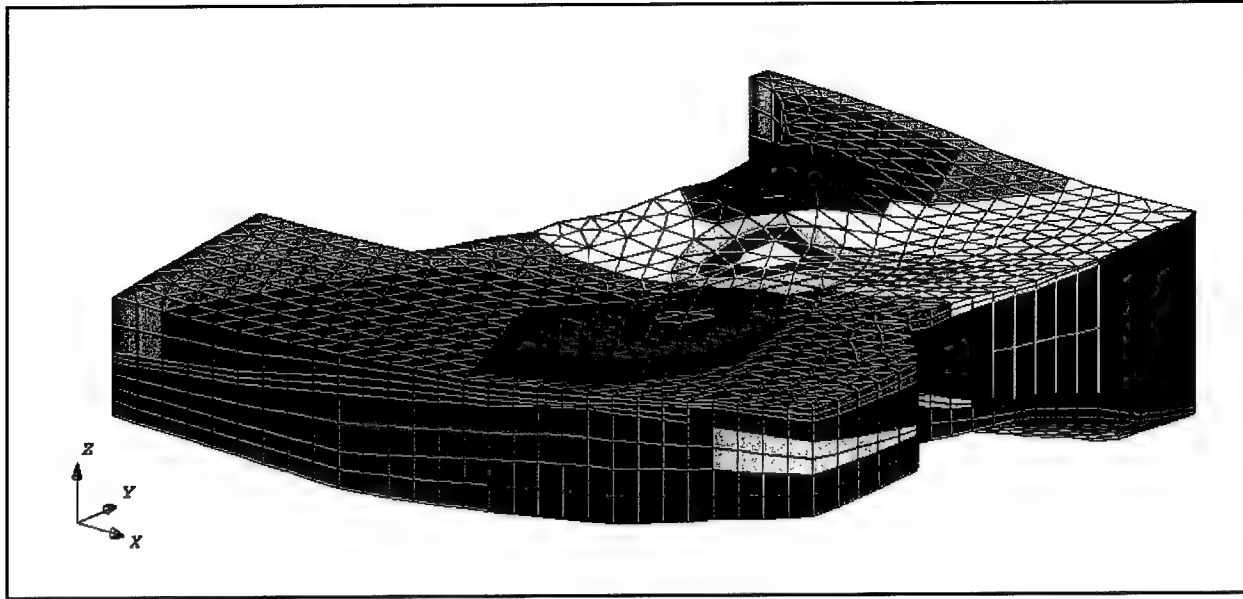


Figure D2. Site heterogeneity illustrated by three-dimensional mesh system used in FEMWATER (colors representing different materials or hydraulic conductivity distribution)

The original and average distribution of subsurface geologic materials were derived from cone penetrometer (CPT) data and interpolated using GMS. Figure D3 illustrates the site subsurface heterogeneity. The material distribution as shown in Figure D4 formed the basis for definition of subsurface layers for modeling purposes.

The numerical model requires flow information at the boundaries of the modeling domain. The water level elevations measured at the monitoring wells were used to estimate transient flow boundary conditions.

The source of flow recharge at Area P was assumed to be solely from rainfall. The precipitation data were collected at Minden, LA (Figure D5). Median values ranged from 6 to 12 cm per month. The rainfall data were used to estimate average infiltration rate for the site.

## Code Description

The model selected for this study, FEMWATER (Lin et al. 1997), is a 3-D finite element numerical code, which may be used to simulate flow and mass transport through saturated-unsaturated media. FEMWATER is an enhanced version of two models, 3DFEMWATER (flow) and 3DLEWASTE (transport). FEMWATER is integrated into GMS (1996). The flow equations in FEMWATER are based on the continuity and Darcy flow equations. The model application is limited by the assumptions applied to these equations relating to laminar flow conditions, incompressible fluid and solid phases, and constant



**Table D1**  
**Hydraulic Conductivity at Cone Penetrometer (CPT) Locations**

CPT Location	Surface Elevation, m	Depth to CPT Point5.54, m	x, m	y, m	z, m	Conductivity m/day <sup>1</sup>
2-1	66.12	18.89	522937.11	208275.66	47.22	9.70
2-3	65.73	5.54	522752.68	208277.31	60.19	0.24
2-5	66.67	12.16	522593.91	208277.33	54.51	0.08
2-5	66.67	7.49	522593.91	208277.33	59.17	0.00
4-4	70.69	18.28	522944.41	208644.91	525.40	6.21
4-4	70.69	6.18	522944.41	208644.91	64.50	0.11
4-4	70.69	15.45	522944.41	208644.91	55.23	1.31
4-4	70.69	20.23	522944.41	208644.91	50.45	11.38
4-4	70.69	4.57	522944.41	208644.91	66.11	2.91
4-5	65.90	15.14	522944.86	208132.76	50.75	0.00
4-5	65.90	20.45	522944.86	208132.76	45.45	9.30
4-5	65.90	15.24	522944.86	208132.76	50.66	2.38
4-5	65.90	14.20	522944.86	208132.76	51.70	3.09
5-1	68.07	6.85	523387.64	207960.94	61.21	0.04
5-1	68.07	16.33	523387.64	207960.94	51.73	0.00
6-1	68.83	11.58	523266.49	208394.07	57.25	1.61
6-1	68.83	7.43	523266.49	208394.07	61.39	1.18
6-1	68.83	14.90	523266.49	208394.07	53.93	3.08
6-2	68.67	10.36	523183.72	208426.06	58.31	9.20
6-2	68.67	12.25	523183.72	208426.06	56.42	3.18
6-2	68.67	17.49	523183.72	208426.06	51.18	1.52
6-3	68.28	6.24	523092.17	208445.32	62.03	3.16
7-1	67.58	16.00	523149.22	208092.33	51.57	0.09
7-1	67.58	7.04	523149.22	208092.33	60.53	0.04
7-1	67.58	4.99	523149.22	208092.33	62.58	0.06
7-2	68.35	17.73	523231.21	208221.28	50.61	0.09
7-2	68.35	10.63	523231.21	208221.28	57.71	3.13

<sup>1</sup> Based on the standard sieve analysis and U.S. Army Corps of Engineers (1960) unified soil classification system.

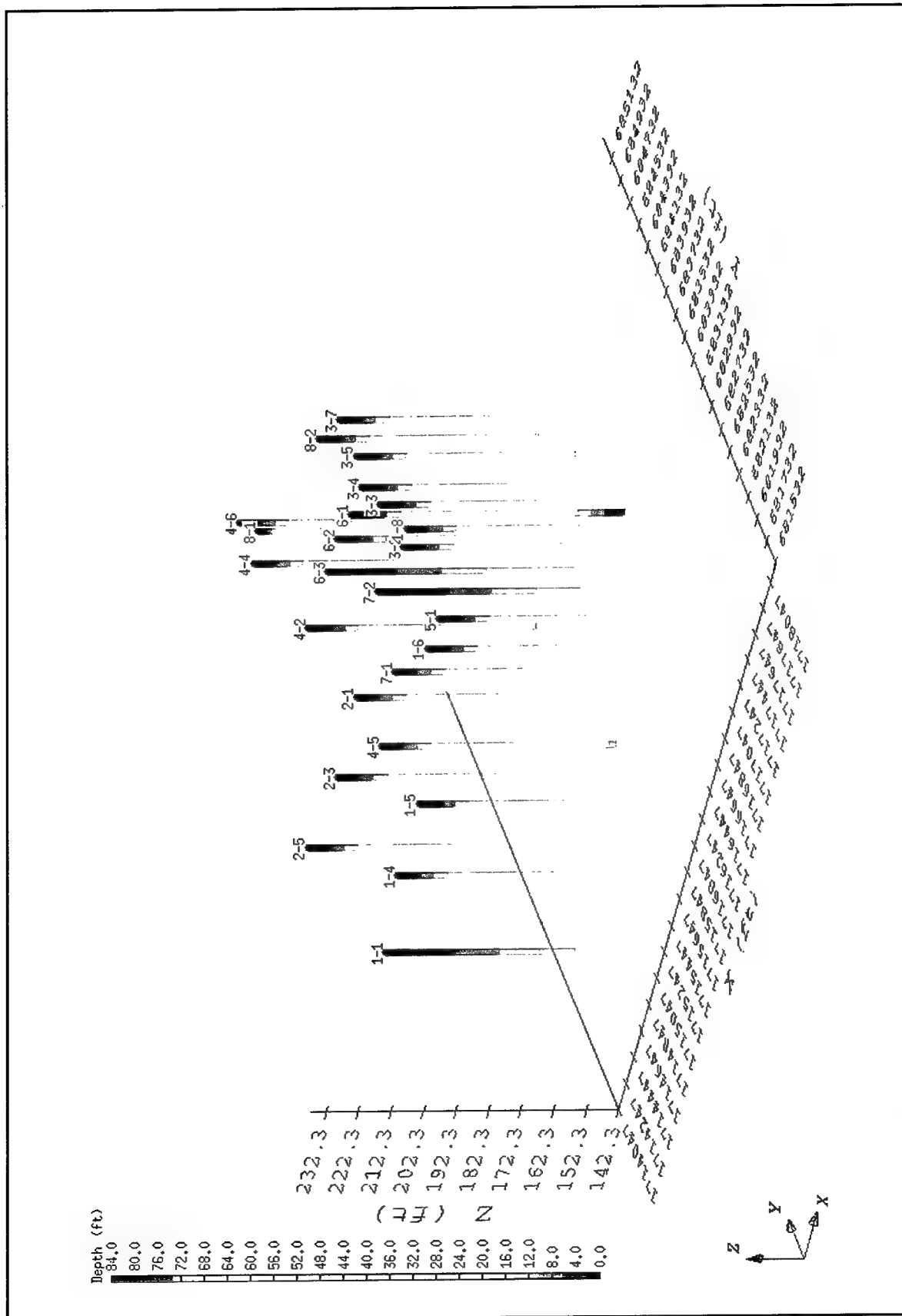


Figure D3. Original stratigraphy distribution based on CPT data (depth of different materials)

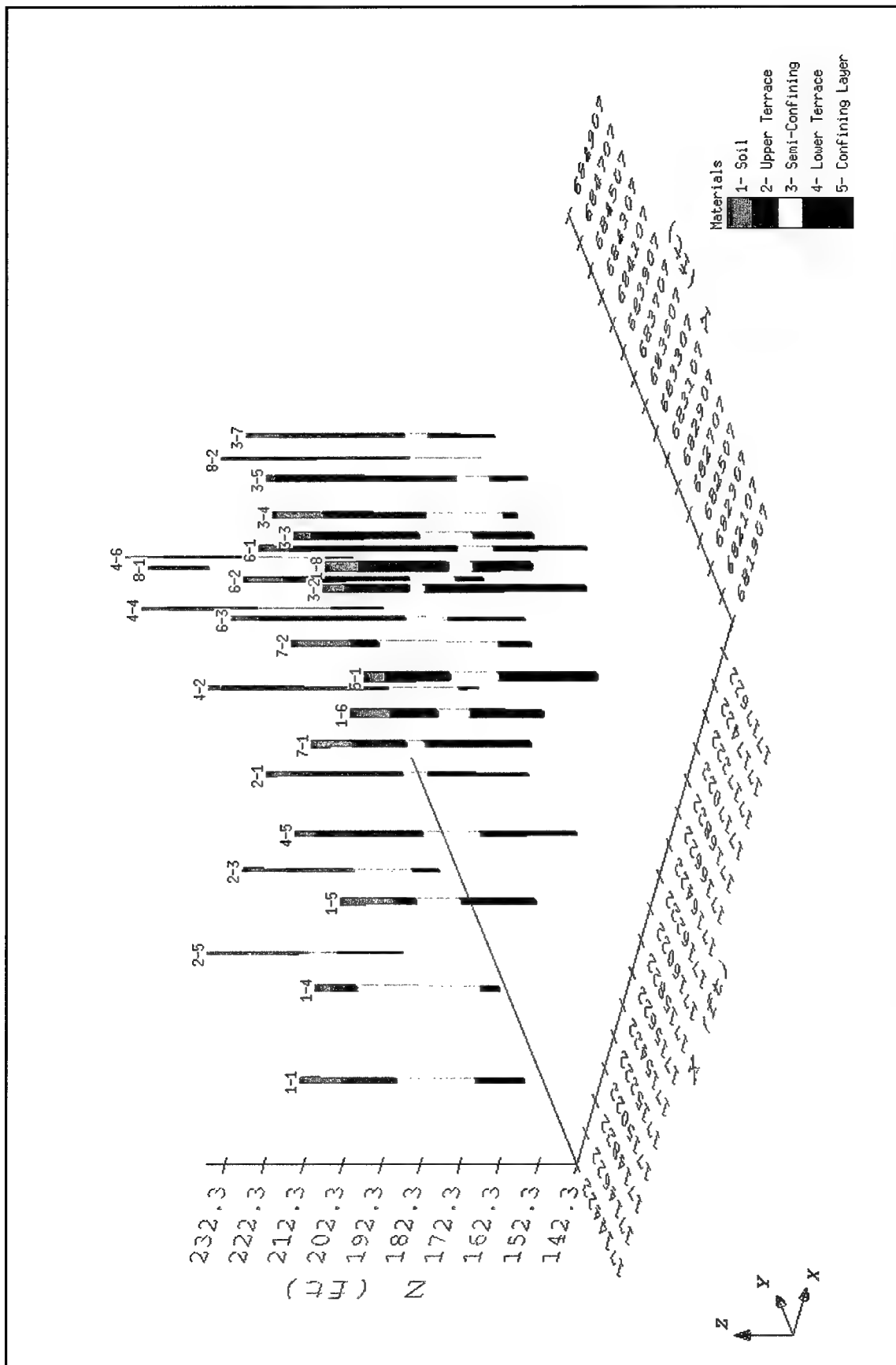


Figure D4. Stratigraphy averaged into five layers at each CPT location (Confining layer (impervious layer) served as a boundary and was not included in model)

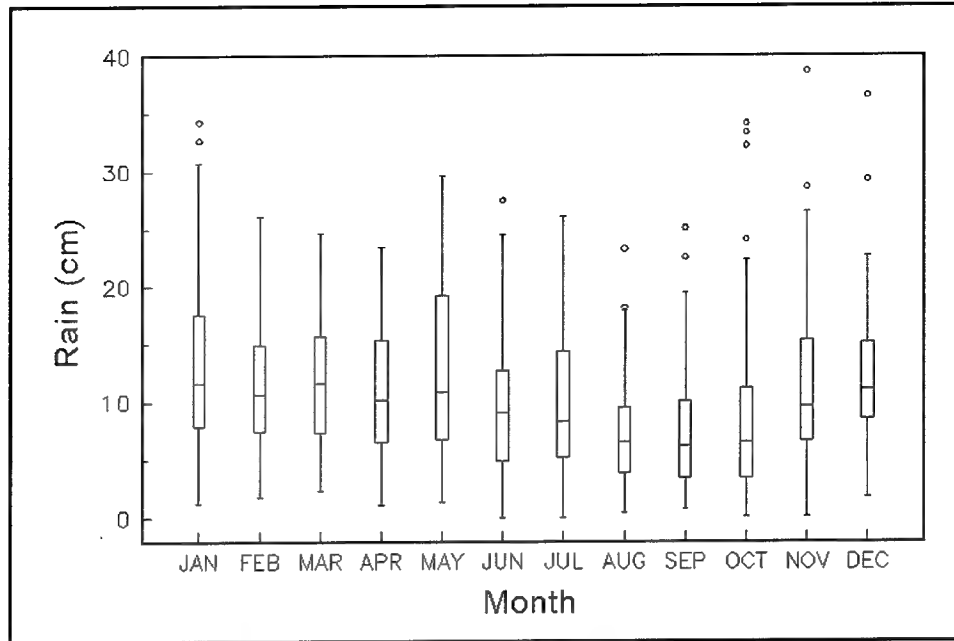


Figure D5. Statistical representation of rainfall data measured at Minde, LA, during 1931-1992 (Horizontal line in each box represents median amount of rainfall per month, and limits of box represent 95-percent confidence interval for each month over time period from 1931 to 1992. Vertical bars represent range of values)

viscosity and density. The Darcy formula (or law) defines the water flow rate ( $Q, L^3/T$ ) in a cylinder filled with sand with cross-sectional Area  $A$  ( $L^2$ ) as:

$$Q = K A \frac{(h_1 - h_2)}{XL} \quad (D1)$$

where

$K$  = hydraulic conductivity ( $L/T$ )

$h_1$  = hydraulic head at upstream (Point 1)

$h_2$  = hydraulic head at downstream of cylinder (Point 2)

$XL$  ( $L$ ) = length of cylinder

FEMWATER simulates the primary processes affecting dissolved-phase contaminant distributions in groundwater including advection, dispersion, sorption, and decay caused by chemical reactions and/or biological transformation. In most groundwater mass transport models, biodegradation in groundwater systems is assumed to follow zero- or first-order decay processes (Kosson, Agnihotri, and Ahlert 1995). In FEMWATER, microbial and

physical/chemical removal mechanisms are collectively represented using an apparent first-order decay rate coefficient.

FEMWATER requires three data sets containing soil parameters for unsaturated-saturated materials. A summary of input and output files used with GMS/FEMWATER are given in Tables D2 and D3, respectively. In unsaturated flow domains, the hydraulic conductivity ( $K$ ) varies with the soil potential head,  $h$ , which is also a function of the volumetric soil moisture content,  $\theta$  (Equations D2 through D4).

<b>Table D2 FEMWATER/GMS Input Files</b>	
<b>File Name</b>	<b>Description</b>
Super File	Text file containing a list of all of the input and output files used in FEMWATER simulation.
Geometry File	Text file containing the data describing the finite element mesh, i.e., node coordinates and element topology.
Mode File	Text file containing analysis parameters and options, material properties, boundary conditions, and initial condition options.
Initial Condition File	Text or binary files containing concentration, pressure head, velocity, moisture content, initial conditions.
Flow File	Text or binary files containing a previously computed flow solution (pressure head and velocity) that are used to define a 3-D flow field for transport-only simulation.

<b>Table D3 FEMWATER/GMS Output File</b>	
<b>File Name</b>	<b>Description</b>
Printed Output	Text file containing a summary of the output.
Pressure Head	Text or binary file containing the computer pressure heads. Used for post-processing or as initial conditions for a subsequent analysis.
Moisture Content	Text or binary file containing the computed moisture content at nodes. Used for postprocessing.
Velocity	Text or binary file containing the computed Darcian velocities. Used for postprocessing.
Concentration	Text or binary file containing the computed concentrations. Used for post-processing or as initial conditions for a subsequent analysis.

Site-specific information for moisture content, relative hydraulic conductivity, and water content is needed to link the input files with the pressure-head distribution. Two options are available in GMS: the user can select an automatic generation of these parameters based on van Genuchten (1980) or input these parameters manually using other available empirical equations such as the one developed by Brooks and Corey (1964). For the LAAP

application described here, Brooks-Corey formulations were selected to allow for representation of each soil type.

### Brooks-Corey formulations

The Brooks-Corey formulations for moisture content, relative hydraulic conductivity, and water content are defined below.

The moisture content ( $\theta$ ), dimensionless, is defined as :

$$\theta = \theta_r + (\phi - \theta_r) * \left( \frac{h_b}{h} \right)^\lambda \quad (D2)$$

and the relative hydraulic conductivity ( $K_r$ , dimensionless) is defined as:

$$K_r = \left( \frac{h_b}{h} \right)^{(2+3\lambda)} \quad (D3)$$

and the water content ( $C_m(h), L^{-1}$ ) is defined as:

$$\begin{aligned} C_m(h) &= -(\phi - \theta_r) * \left( \frac{\lambda}{h_b} \right) * \left( \frac{h}{h_b} \right)^{-(\lambda+1)} & \text{for } h \leq h_b \\ C_m(h) &= 0 & \text{for } h > h_b \end{aligned} \quad (D4)$$

where

$\theta_r$  = residual moisture content (dimensionless)

$\phi$  = porosity (dimensionless)

$h_b$  = bubbling or air-entry pressure ( $L$ )

$h$  = pressure head ( $L$ )<sup>1</sup>

$\lambda$  = pore size distribution index, which is a function of soil texture (dimensionless)

To evaluate the parameters used in Equations D2-D4, published values for soil types that match site soil characteristics are normally used. Saturated hydraulic conductivity data (Site Subsurface Soil, Table D1) were ranked into six classes of materials to match the Brooks and Corey (1964) parameters given in Table D4. These parameters were used in the above equations to calculate required unsaturated soil input data. An alternative approach is to determine

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<sup>1</sup> The uppercase letters,  $L$ ,  $T$ , and  $M$  are used to denote generic length, time, and mass units.

**Table D4**  
**Brooks and Corey (1964) Parameters Used in the Model**

Soil Type	Saturated Hydraulic Conductivity $K$ , m/day	Site Hydraulic Conductivity Range, m/day	$\phi$	$\theta_r$	$-h_b$	$\lambda$
Unconsolidated sand	8.5	9.20 - 11.4	0.424	0.09	0.114	4.4
Sand	8.2	6.2	0.435	0	0.196	0.84
Fine sand	2.1	2.3 - 3.2	0.377	0.06	0.82	3.7
Columbia sandy loam	0.7	1.18 - 1.6	0.496	0.11	0.85	1.6
Touchet silt loam	0.22	0.02 - 0.11	0.43	0.1	1.45	1.7
Hygiene sand stone	0.15	0.0031	0.25	0.13	1.06	2.9

these parameters from the best-fit line through the data points of pressure head versus effective saturation. The slope of the line represents  $\lambda$ , and its intercept at full saturation represents  $h_b$ . However, collection of appropriate data is frequently impractical due to cost and time constraints. The use of Brooks and Corey parameters provides a reasonable input for the model in the absence of adequate site data.

### Transport equations

The governing equation for the transport part of FEMWATER is based on continuity of mass and advection/diffusion laws:

$$\theta_w \frac{\partial C}{\partial t} + \rho_b \frac{\partial S}{\partial t} + V \cdot \nabla C = \nabla \cdot (\theta_w D \cdot \nabla C) - \kappa (\theta_w C + \rho_b S) + Q C_{in} - \left[ \frac{\rho^*}{\rho} Q - \frac{\rho_0}{\rho} V \cdot \nabla \left( \frac{\rho}{\rho_0} \right) \right] C \quad (D5)$$

$$S = K_d C \quad \text{linear isotherm}$$

$$S = \frac{S_{\max} K_L C}{1 + K_L C} \quad \text{Langmuir isotherm} \quad (D6)$$

$$S = K_F C^n \quad \text{Freundlich isotherm}$$

where

$\theta_w$  = moisture content (dimensionless)

$C$  = aqueous phase concentration ( $M/L^3$ )

$t$  = time

$\rho_b$  = bulk density of medium ( $M/L^3$ )

$S$  = solid (or adsorbed) phase concentration ( $M/M$ )

$V$  = flow velocity ( $L/T$ )

$\nabla$  = del operator

$D$  = dispersion coefficient tensor ( $L^2/T$ )

$\kappa$  = decay rate ( $1/T$ )

$Q$  = volume flow rate per unit volume of source or sink ( $1/T$ )

$C_{in}$  = source or sink concentration

$\rho^*$  = density of injected fluid ( $M/L^3$ )

$K_d$  = distribution coefficient ( $L^3/M$ )

$S_{max}$  and  $K_L$  = maximum absorbed concentration allowed in medium ( $M/M$ )  
and constant coefficient in Langmuir nonlinear isotherm,  
respectively

$K_F$  and  $n$  = coefficient and power constant for Freundlich nonlinear  
isotherm, respectively

The dispersion coefficient tensor  $D$  ( $L^2/T$ ) in Equation 4 is given as:

$$\theta_w D = a_T |V| \delta + (a_L - a_T) \frac{VV}{|V|} + a_m \theta_w \tau \delta \quad (D7)$$

where

$|V|$  = magnitude of vector velocity,  $V$  ( $L/T$ )

$\delta$  = Kronecker delta tensor

$a_T$  = lateral dispersivity ( $L$ )

$a_L$  = longitudinal dispersivity ( $L$ )

$a_m$  = molecular diffusion coefficient ( $L^2/T$ )

$\tau$  = tortuosity

### Model limitations

Major assumptions and limitations of FEMWATER include the following:

- (a) single constituent transport, thus intersolute reactions cannot be simulated,
- (b) abiotic and microbial degradation is treated with a first-order decay model,
- (c) adsorption coefficient and decay rates can be assigned for different



subsurface materials; however, rate constants do not change during simulation time, (d) contaminant sorption is instantaneous and reversible, and the adsorbed phase is in local equilibrium, (e) microbial biomass production, fate and transport of electron acceptors, and cometabolic degradation are not included in FEMWATER. A new code (3DFATMIC) has been developed based on FEMWATER, which includes options for more detailed calculations; however, the input data requirements are more complex (U.S. Environmental Protection Agency (EPA) 1997a).

For the LAAP site, the above assumptions were substantiated by introducing some simplifications of the site characteristics. For more details, the reader is referred to FEMWATER model theory documentation (Lin et al. 1997).

## **Model Construction**

FEMWATER requires basic hydrogeologic and chemical data for its simulations. The input data include hydraulic conductivity, porosity, hydraulic gradient, infiltration rate, initial and boundary conditions, distribution (partition) coefficient, and decay rates. The distribution coefficient  $K_d$  relates the sorbate and solute for linear isotherms.

### **Modeling domain**

In plane view, the modeling domain is bounded by D-Line on the west and Pearl Harbor Avenue on the east. In the vertical direction, the modeling domain includes the Upper Terrace and the Lower Terrace Aquifers (Figures D3 and D4). The 3-D mesh for this site (Figure D2) was constructed by first dividing the surface domain into uniform triangular elements and then adding the subsurface layers into the mesh. For detailed information on mesh generation, the reader is referred to the GMS users's manual (1996).

The modeling domain does not cover any physical boundaries such as streams. However, FEMWATER requires numerical flow data at the boundaries. The water-level elevation data collected at the monitoring wells were used to generate boundary data for the model. The water-level data were collected in both the Upper Terrace and the Lower Terrace Aquifer. Two-dimensional interpolation tools of GMS were used to create contours of water-level elevation in both aquifers. The intersection between these contours and boundaries provided the boundary-condition values.

Other required parameters in FEMWATER include convergence criteria and coefficients of numerical solution techniques. One of the parameters that controls the amount of leachate entering the unsaturated zone is the infiltration rate. The infiltration rate is usually calculated from precipitation data and soil characteristics. The precipitation data collected at Minden was used to estimate infiltration rates (Figure D5).

Another parameter, hydrodynamic dispersion (i.e., the spreading and mixing caused by mechanical dispersion) was introduced in FEMWATER in terms of dispersivity ( $\alpha$ ). The field values for dispersivity normally are unknown and difficult to obtain. These parameters are strongly scale dependent and vary with site dimensions (Electric Power Research Institute 1985). In this study, dispersivities were adopted from values reported for other sites with similar characteristics. Reported values for dispersivities include 21.3 m longitudinally and 4.27 m transversely for the glacial outwash aquifer consisting of beds of fine and coarse sand, gravel, and silt in Long Island, New York (Pinder 1973) and 0.6 m longitudinally for the Bunter Sandstone aquifer near Mansfield, England (Oakes and Edworthy 1976).

In this application, the following values for dispersivity were used because the measured values were unavailable. Adjustment of the dispersivity values during model calibration is possible.

$$\begin{aligned}\alpha_L &= 21.3 \text{ m} \approx 70 \text{ ft} \\ \alpha_T &= 4.27 \text{ m} \approx 14 \text{ ft}\end{aligned}\tag{D8}$$

### Retardation factor

In mathematical modeling, contaminant adsorption is based on the concept of the retardation factor  $R$  as:

$$R = \frac{u}{u_s}\tag{D9}$$

where

$u$  = mean water velocity ( $L/T$ )

$u_s$  = mean chemical (solute) velocity ( $L/T$ )

The retardation factor provides a general indication of the mobility of a contaminant in the soil. Hartley and Graham-Bryce (1980) have shown that  $R$  (dimensionless) is equivalent to the ratio of total concentration ( $C_t$ ,  $M/L^3$ ) to dissolved concentration ( $C_w$ ,  $M/L^3$ ) of contaminant.

$$\begin{aligned}C_t &= \text{Dissolved} + \text{Adsorbed} \\ C_t &= C_w \cdot \phi \cdot S_w + C_s \cdot \rho_B\end{aligned}\tag{D10}$$

where

$C_s$  = concentration of chemical adsorbed to solid particles ( $M/M$ )

$\rho_B$  = bulk density ( $M/L^3$ )

$\phi$  = porosity

$S_w$  = water saturation (volume of water/volume of voids)

$\phi S_w$  = moisture content (volume of water/bulk volume)

If linear equilibrium adsorption is assumed as described earlier, then the retardation factor  $R$  due to adsorption is given as:

$$R = \frac{C_w \phi S_w + C_s \rho_B}{C_w \phi S_w} = 1 + \frac{C_s \rho_B}{C_w \phi S_w} = 1 + \frac{K_d \rho_B}{\phi S_w} \quad (D11)$$

Hence, the retardation factor is a function of chemical sorption ( $K_d$ ) and soil properties ( $\rho_B$ ,  $\phi$ ,  $S_w$ ).

### Adsorption coefficients

Results from laboratory batch testing for adsorption of explosives (TNT and RDX) compounds to LAAP soils were used to develop input data for modeling purposes. The initial exposure of uncontaminated soil to TNT and RDX could represent the soil response to the contamination front as it migrates through the aquifer. The rates of laboratory-measured sorption of TNT and RDX were about two orders of magnitude faster than the microbial mineralization. Pseudo-equilibrium of TNT and RDX with LAAP soils was reached within a few days. After equilibrium, the removal rate was dominated by the microbial activity. Adsorption coefficients for TNT and RDX in LAAP soils are presented in Table D5. The  $K_d$  values for TNT ranged from 0.08 to 0.33 L/kg depending on

**Table D5**  
**Explosives Adsorption Coefficients ( $K_d$  L/kg) for LAAP Aquifer Soils and Regression Coefficient ( $r^2$ )<sup>1</sup>**

Compound	ML Soil		SP-SM Soil		CL Soil		SM Soil	
	$K_d$	$r^2$	$K_d$	$r^2$	$K_d$	$r^2$	$K_d$	$r^2$
TNT	0.33	0.96	0.23	0.99	0.27	0.92	0.08	0.90
RDX	0.21	0.95	0.33	0.97	0.33	0.83	0.33	0.95

<sup>1</sup> Batch tests conducted under aerobic conditions.

the type of soil. For RDX, the values ranged from 0.21 to 0.33 L/kg. An average value of 0.228 L/kg for TNT and 0.30 L/kg for RDX were used for the modeling.

## Decay rates

A critical input to the model is an estimate of the rate of contaminant decay or removal that is reflective of the dominant biogeochemical pathways at the site. Direct measurement of in situ rates of microbial degradation currently is not possible. One approach to measure the degradation rates is to sample aquifer sediments and monitor contaminant disappearance as a function of time testing using batch or column reactors operated under controlled laboratory conditions. Alternatively, the use of radiorespirometric techniques can be applied to measure microbial degradation. Radiorespirometry tests indicate the potential for complete mineralization to occur. The actual rate in the groundwater would differ from laboratory tests due to inherent differences in the amount of biomass present, temperature, the presence of electron acceptors, and mass transfer limitations. The laboratory approach introduces uncertainties (Madsen 1991) and may greatly overestimate rates of microbial metabolism in some groundwater systems (Chapelle and Loveley 1990). In the batch tests, mass transport limitations are eliminated, and the mixing conditions promote more effective contact between aquifer materials and groundwater than can be achieved in the field. Laboratory tests represent the potential rate of degradation in the absence of mass transport limitations.

The decay rates from the laboratory batch studies and radiorespirometric studies on the LAAP soils are given in Tables D6 and D7. The batch tests were conducted using uncontaminated LAAP soils exposed to LAAP groundwater contaminated with TNT and RDX (90 g soil/360 g water). As shown in Table D6, the apparent rate constants (batch tests) ranged from 0.01 to 0.03 day<sup>-1</sup>, with corresponding half-lives on the order of months. It is important to note the difficulty in developing this type of data due to the heterogeneity of the soil and the complexity of physical and chemical interactions in a multicomponent system. The radiorespirometric data are based on mineralization of a 30-percent slurry of LAAP soil exposed to either TNT (2 mg/L) or RDX (21 mg/L). The apparent rate constants from radiorespirometry are one to two orders of magnitude lower than the batch testing results with half-lives ranging from 1 to 10 years (Table D7). In general, the highest rates of removal were associated with clay soils.

**Table D6**  
**Summary of Apparent First-Order Removal Rate Constants for Uptake of TNT and RDX from Groundwater on Uncontaminated LAAP Soils<sup>1</sup>**

Soil Type	TNT		RDX	
	Decay Rate Constant, k, d <sup>-1</sup>	Half-Life, days	Decay Rate Constant, k, d <sup>-1</sup>	Half-Life, days
Sandy silt (ML)	0.014	48	<0.002	>350
Sandy silt (SP-SM)	0.014	48	<0.002	>350
Lean clay (CL)	0.034	20	<0.002	>350
Silty sand (SM)	0.017	42	<0.002	>350

<sup>1</sup> Water source was MW085u; results are from batch tests conducted under anaerobic conditions; initial concentrations were approximately 8 and 10 mg TNT and RDX L<sup>-1</sup>, respectively.

<b>Table D7</b> <b>Summary of Apparent First-Order Microbial Mineralization Rate Constants for Degradation of TNT and RDX in LAAP Soils<sup>1</sup></b>				
Soil Type	TNT		RDX	
	Radiorespirometry Rate Constant, $k$ , $d^{-1}$	Half-Life, days	Radiorespirometry Rate Constant, $k$ , $d^{-1}$	Half-Life, days
Sandy silt (ML)	$5.7 \times 10^{-4}$ to $2.2 \times 10^{-3}$	320 to 1,220	$1.8 \times 10^{-4}$	3,850
Sandy silt (SP-SM)	$4.6 \times 10^{-4}$	1,510	$5 \times 10^{-4}$	1,390
Lean clay (CL)	$<1 \times 10^{-4}$	>3,900	$<1 \times 10^{-4}$	>3,900
Silty sand (SM)	$<1 \times 10^{-4}$	>3,900	$2 \times 10^{-3}$	323
<sup>1</sup> Radiorespirometry tests were run at $23.3 \pm 3.2$ °C under aerobic conditions. Initial aqueous phase concentrations were 2 and 21 mg TNT and RDX $L^{-1}$ , respectively.				

The capacity of the soil to support biological degradation varies slightly over the site due to physical chemical properties of the soils. Also note that the detection limit for measurement of microbial rate constants is about  $10^{-4} \text{ day}^{-1}$  for radiorespirometry test and is about  $0.002 \text{ day}^{-1}$  for batch test. These are other reasons for discrepancies between the rates used in the model and those from the laboratory tests. The rates from radiorespirometry tests would simulate conditions where microbial mineralization was the dominant removal mechanism. This situation would exist within the contaminant plume where the aquifer solids are in quasi-equilibrium with the groundwater. The batch tests would simulate uptake rates at the edge of the plume where uncontaminated soils are initially exposed to TNT and RDX (Table D6). Because the LAAP site has a history of over 40 years of exposure to explosives, microbial degradation is likely to be the dominant factor controlling the removal rate. Therefore, the decay rates from radiorespirometry were used as initial model inputs.

The field data represent the change in contaminant concentration at specific locations at the site and incorporate all removal mechanisms and mass transport limitations. The decay rates used in the model were determined based on the radiorespirometry results (Table D7) and model calibration using field concentration data. The values used in the model were  $10^{-5} \text{ day}^{-1}$  (half-life of 190 years) for TNT and  $8.13 \times 10^{-6} \text{ day}^{-1}$  (half-life of 233 years) for RDX.

## Initial Flow and Concentration Distributions

The modeling domain consisted of Area P and vicinity. The modeling focused on transport of TNT and RDX. Initial conditions of flow and contaminant concentration play a major role in model outcomes. Different numerical techniques available in GMS were compared to establish realistic initial flow and mass concentration distributions at the site. The amount of

explosives originally dumped at the site is unknown. Therefore, for the modeling exercise described here, the first round of the water-level elevations and concentrations (TNT and RDX) data collected in February 1996 were used as initial conditions for flow and mass transport calculations of the model, respectively. The GMS was used to interpolate/extrapolate the data for all points of the numerical mesh system.

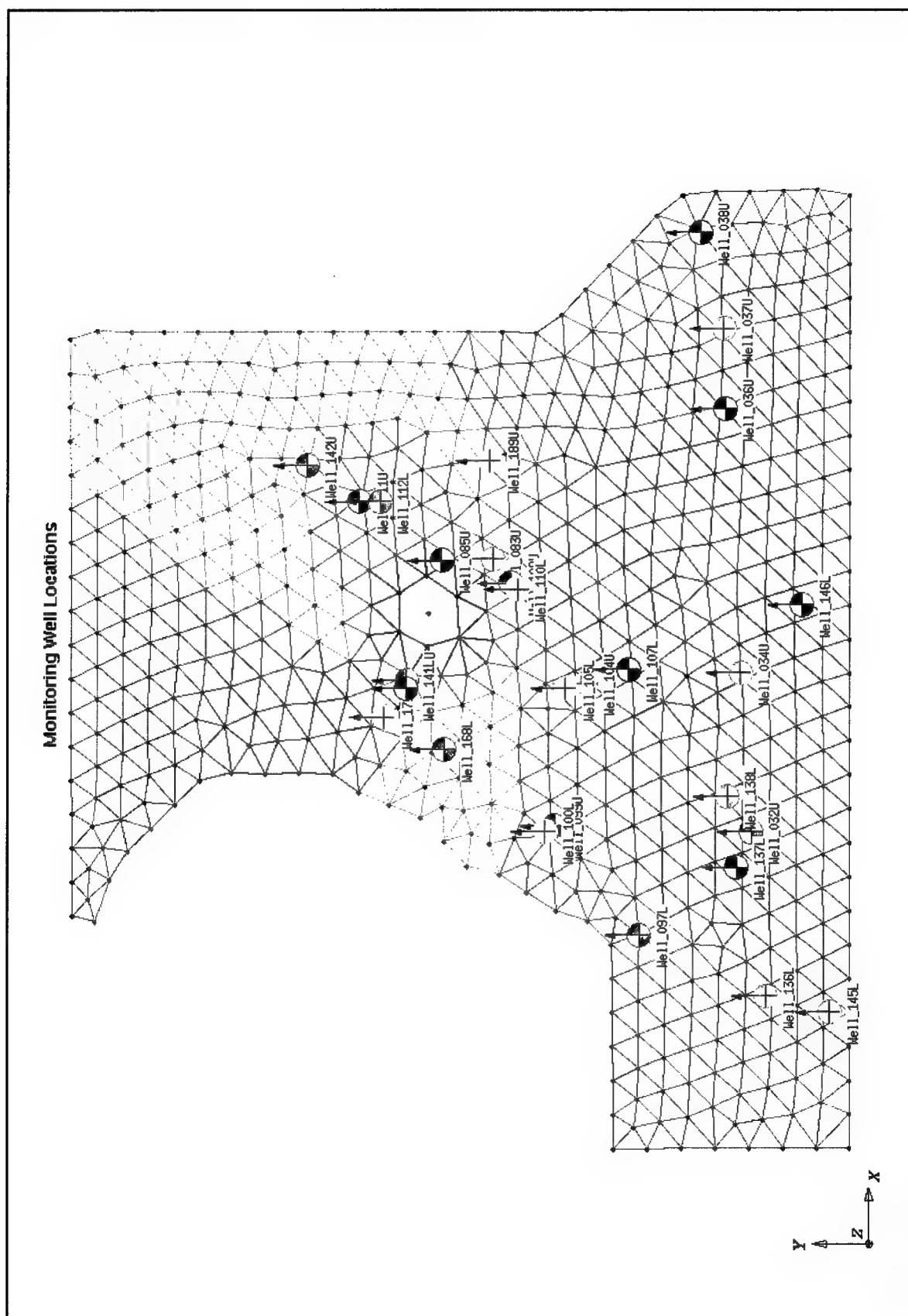
## Calibration

Numerical flow models are calibrated by adjusting values of hydraulic conductivity, boundary conditions, and recharge rates and their distribution so that a reasonable match between the simulated and measured hydraulic head is achieved in spite of any possible measurement errors. The transport model is calibrated by adjusting adsorption rates, decay rates, and dispersion parameters.

For the LAAP site, the calibration process was carried out by manual trial and error. The calibration included varying parameters such as flow boundary conditions, hydraulic conductivity distributions, and infiltration rates until a reasonable match between observed and simulated flow conditions at monitoring wells was obtained. GMS 2.0, used here, has an option called Gages Tool that was used to compare the simulated and measured results (in GMS 2.1 Map Module has a similar function). Figure D6 illustrates the location of the gauges (monitoring wells) used in the model calibration. The simulated and measured water-level elevation and TNT and RDX concentration at selected monitoring wells were compared. The simulated and measured total head (water-level elevation) at MW037U (downstream and screened in the Upper Terrace Aquifer), MW138L (downstream and screened in the Lower Terrace Aquifer), and MW142U (upstream and screened in the Upper Terrace Aquifer) are shown in Figures D7 through D9. As illustrated in these figures, the model is able to simulate the head at these locations even though the site hydrogeology is fairly complex. The maximum difference between the simulated and measured head is about 0.9 m (3 ft).

The hydraulic conductivity of the site has a major effect on the flow calibration compared with the other parameters mentioned earlier. Therefore, additional data to define the spatial variability of hydraulic conductivity at the LAAP site would help in reconciling the simulated results with the measured values.

The accuracy of the transport model of explosives is controlled by both flow and chemical data. After the flow model is calibrated, the transport model must be calibrated using site-specific chemical input data. The major parameter that influences the ability of FEMWATER to predict explosive (transport) is the first-order decay rate. The model was calibrated using this rate. A representative simulated and measured concentration of TNT and RDX over 400 days of simulations are given in Figure D10 (representing a high concentration of TNT) and D11 (representing a high concentration of RDX). As illustrated in



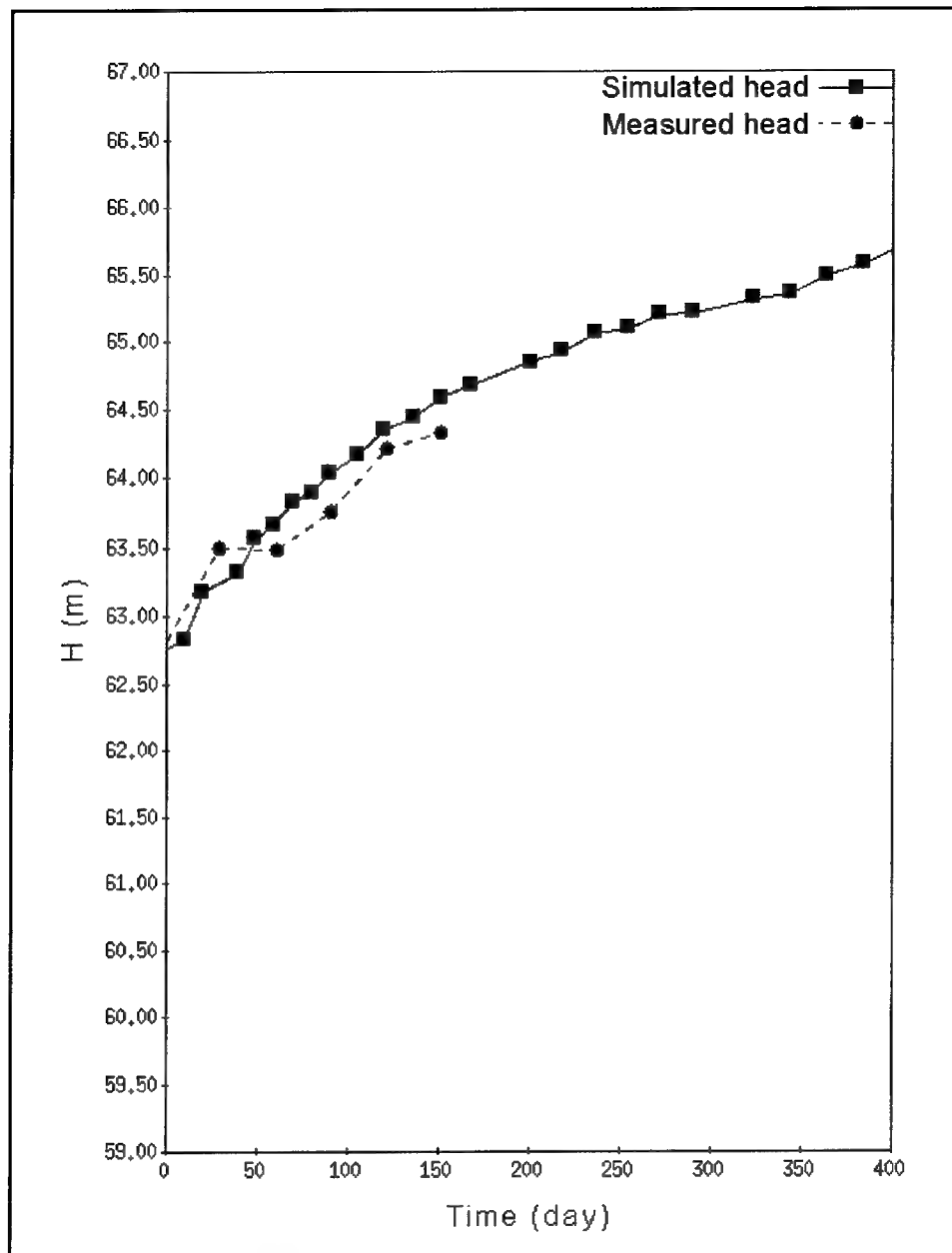


Figure D7. Comparison between measured (---●---) and simulated (---■---) head (m, above MSL) in MW037U screened in Upper Aquifer

Figure D10, the difference between the simulated and measured TNT concentrations are reasonable and display similar trends of reduction. For RDX (Figure D11), at the beginning of the simulation, the differences between the simulated and measured concentrations is about  $2,000 \mu\text{g L}^{-1}$ , but as the time advances, the differences were reduced. One reason for this discrepancy is that interpolation/extrapolation of the initial conditions might not have captured the actual measured initial concentration of RDX at this monitoring well. The simulated and measured RDX concentrations have similar trends of reduction, which affects the long-term prediction. The long-term prediction of the plume is



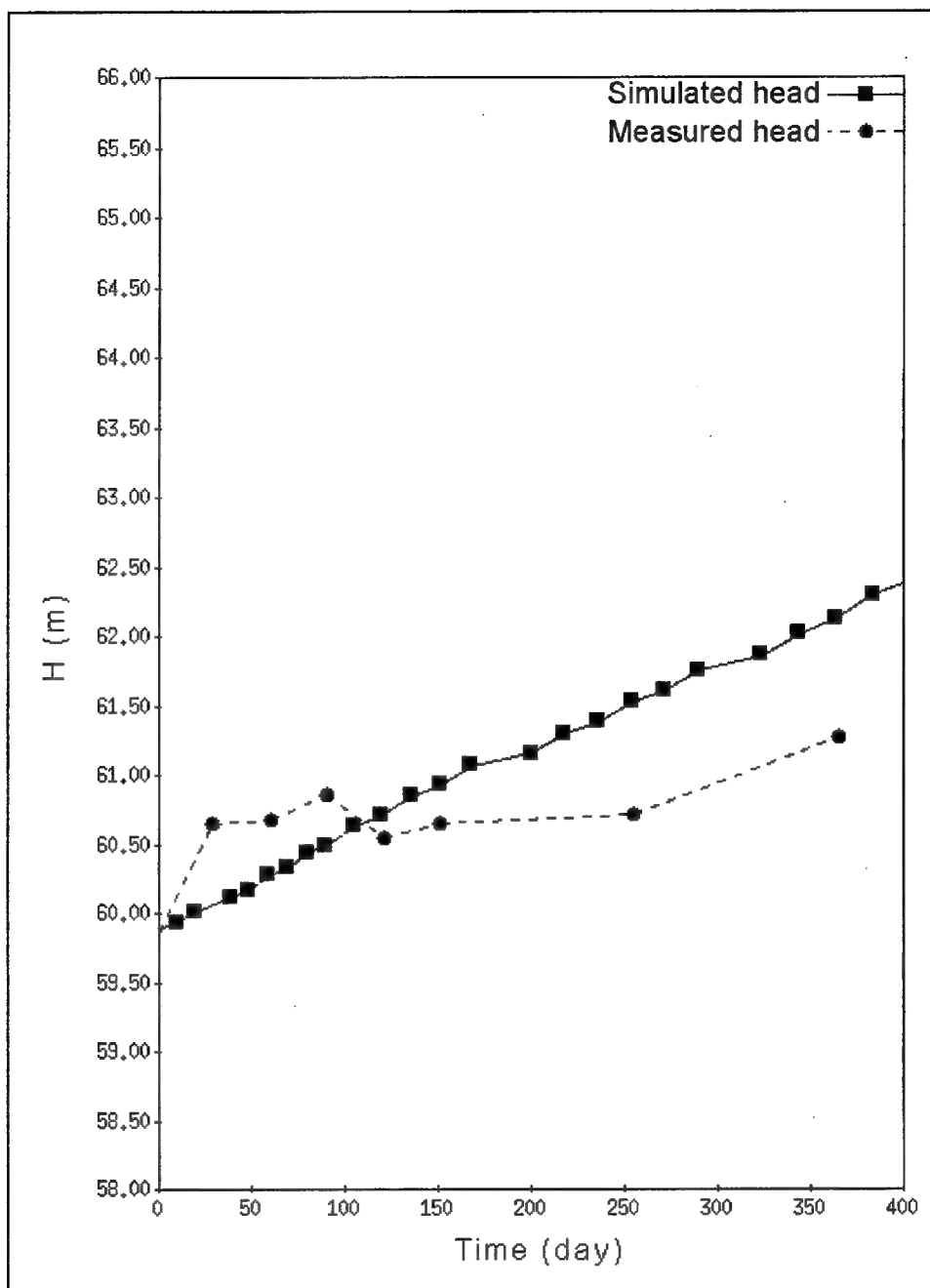


Figure D8. Comparison between measured (---●---) and simulated (---■---) head (above MSL) in MW138L screened in Lower Aquifer

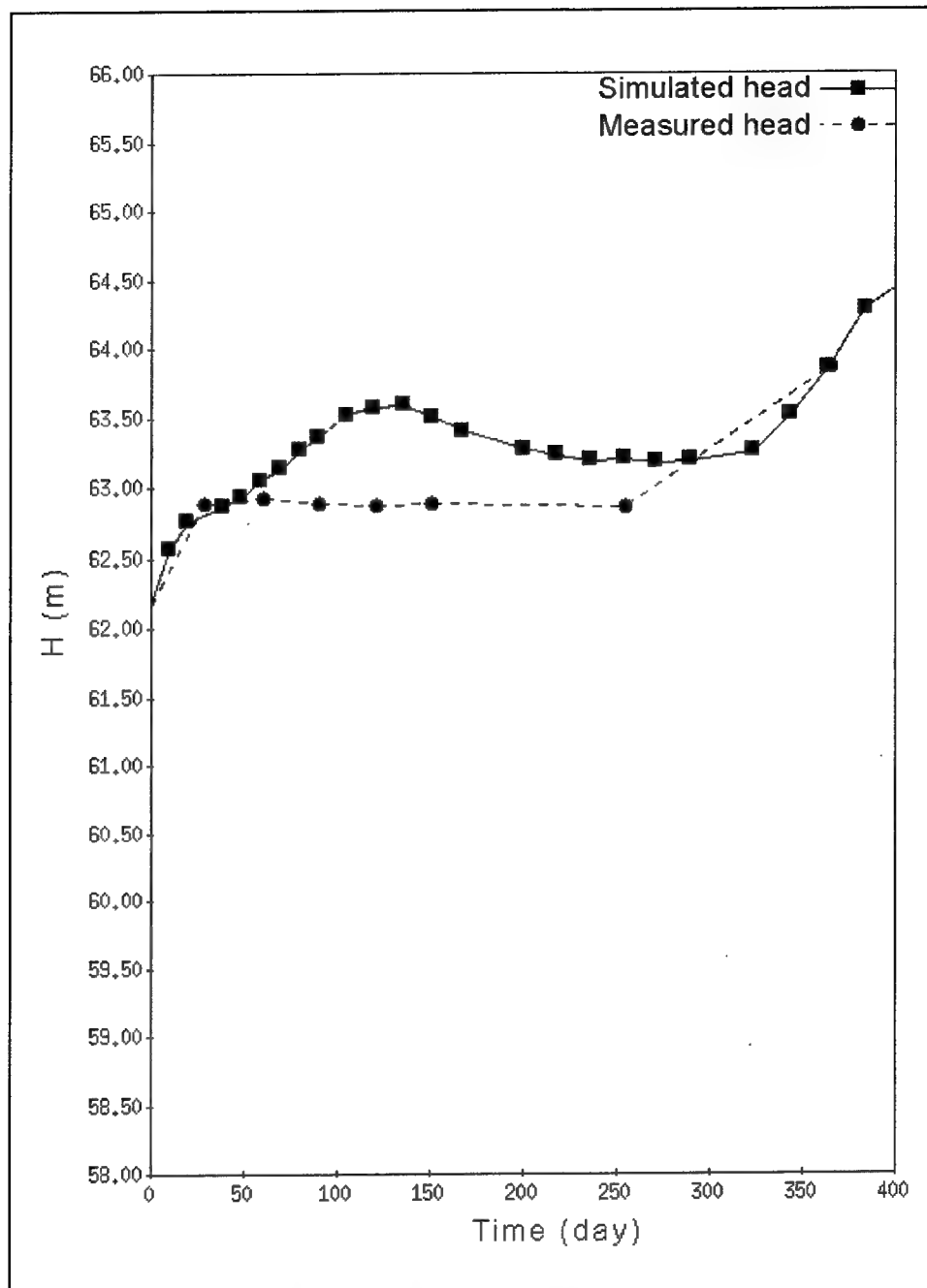


Figure D9. Comparison between measured (---●---) and simulated (---■---) head (above MSL) in MW142U screened in Upper Aquifer

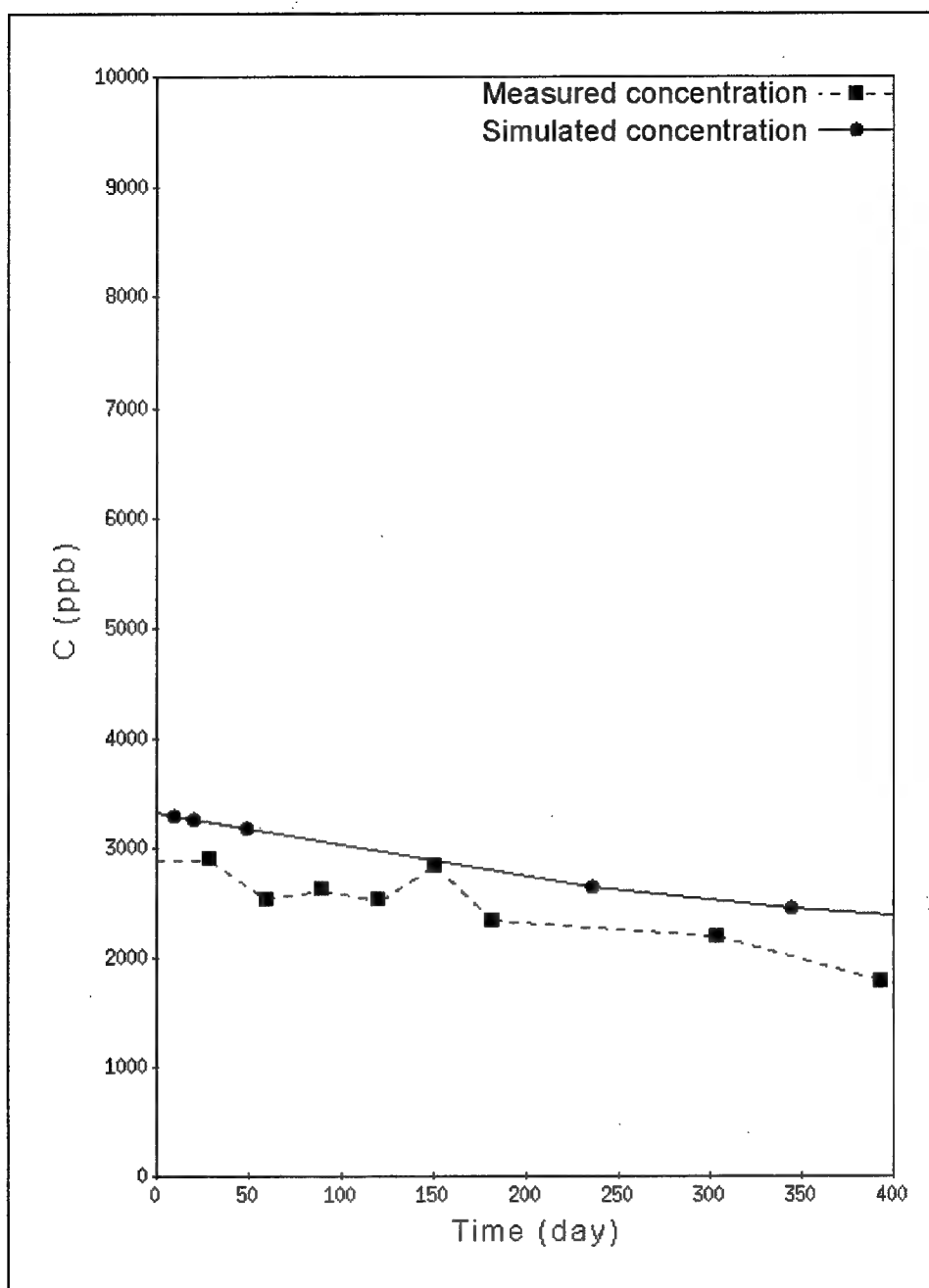


Figure D10. Simulated (---●---) and measured (---■---) TNT concentration in MW083U versus time

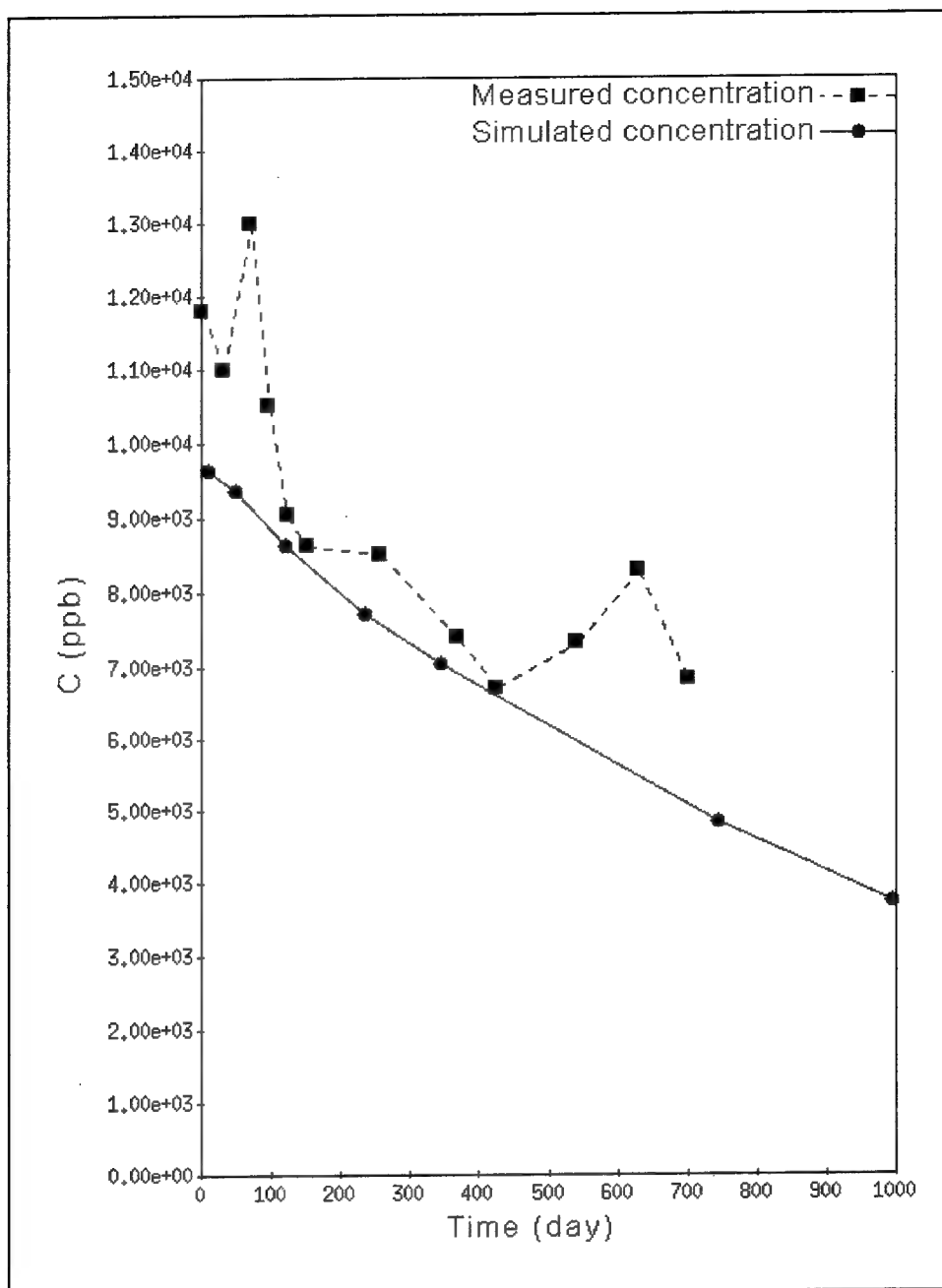


Figure D11. Simulated (—●—) and measured (---■---) RDX concentration in MW083U versus time

important in evaluating the ultimate outcome of natural attenuation at this site. The calibrated models were applied to development of long-term predictions of TNT and RDX fate and transport.

## Sensitivity Analysis

The sensitivity of the model simulations and predictions coupled with the desired level of accuracy determine the level of detail required for field and laboratory measurements that are used for model input. A model that is not sensitive to a specific input parameter may produce the same output regardless of input changes. On the other hand, the more sensitive the model is to a parameter, the effort to estimate that parameter correctly will be greater.

Sensitivity analysis for a particular model may be performed in several ways. The simplest approach, which is applicable to all numerical models and exercised here, is to determine the effect of changing the value of each input parameter on the output by varying model inputs systematically.

The model was evaluated for its sensitivity to changes in the values of hydraulic conductivity, adsorption coefficient, and decay rate. The hydraulic conductivities were increased and decreased by an arbitrary value of 10 percent, and the results for TNT concentration were compared. Figure D12 shows the time series of measured TNT concentrations along with simulated results of three scenarios with different hydraulic conductivities at MW083U screened in the Upper Terrace Aquifer. Increasing or decreasing the hydraulic conductivity by 10 percent did not significantly impact the modeled results. The reason for the apparent lack of sensitivity to the hydraulic conductivity is due to the relatively low conductivity associated with this site. This indicates that the model is moderately sensitive to the changes of the hydraulic conductivity at the LAAP site.

The sensitivity of the model to the adsorption coefficient is shown in Figure D13. One order of magnitude change of the adsorption coefficient from 0.23 to 2.3 L/kg caused about 40-percent change in TNT concentration at the end of 1,000 days of the simulations. Increased adsorption results in lower overall decay of TNT concentration in the groundwater during 1,000 days of the simulation for the range of values considered here. The extent of adsorption on LAAP soils is quite low relative to other soil types. This indicates that the model is sensitive to the adsorption coefficient.

The sensitivity analysis of the model to decay rate was tested by varying the decay rate from  $10^{-5}$  to  $10^{-4}$  day<sup>-1</sup> while holding adsorption and conductivity constant. About 12-percent change was observed in the predicted TNT concentration at the end of 1,000 days simulations (Figure D14). This indicates that the model is moderately sensitive to the decay rate.

Refinements in the understanding of the interplay between adsorption and degradation would improve the accuracy of the model simulations.

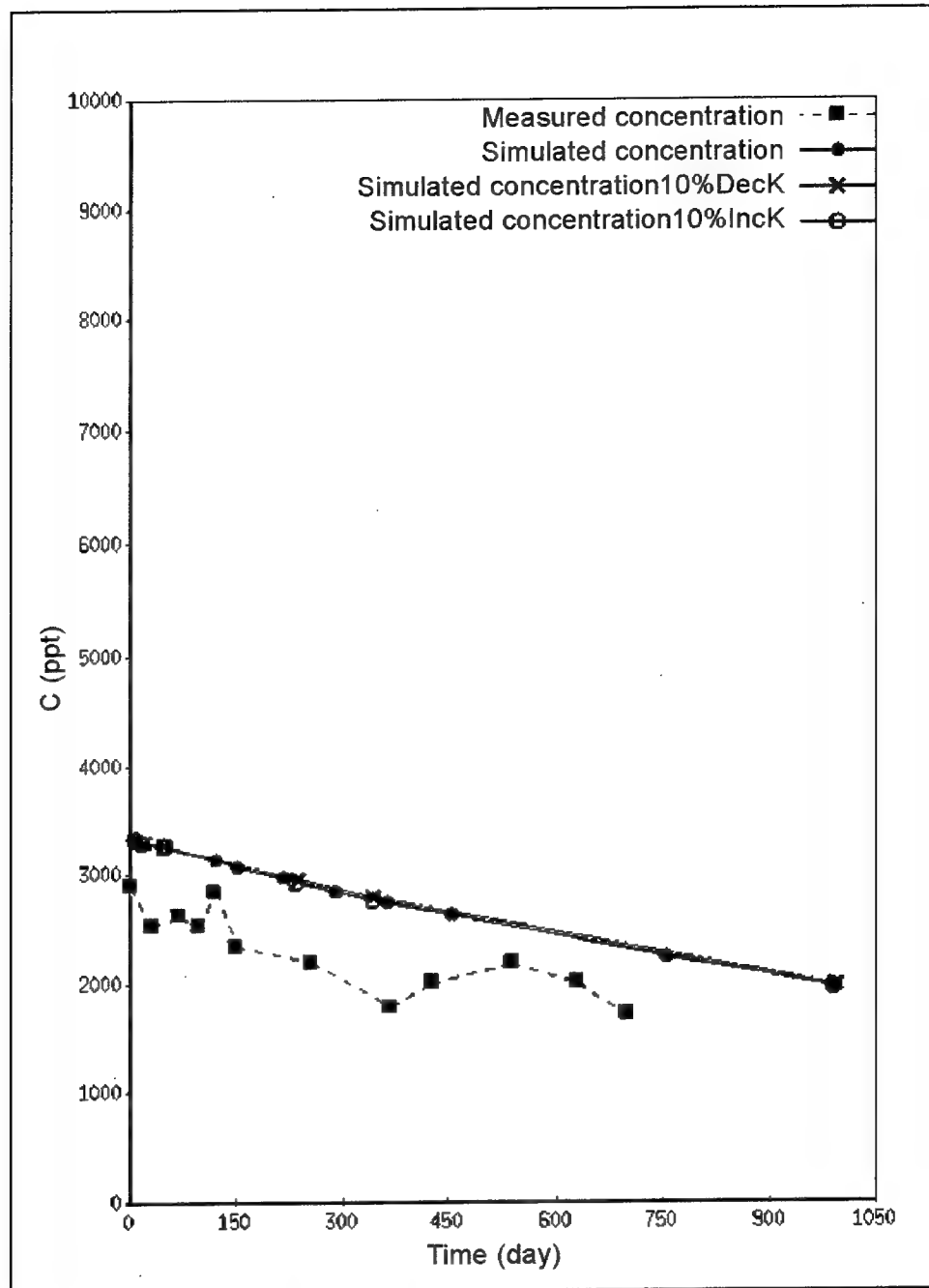


Figure D12. Time series of TNT concentration for measured, calibrated model, calibrated model with 10-percent increase of conductivity, and with 10-percent decrease of conductivity, respectively (Original data were from MW083U)

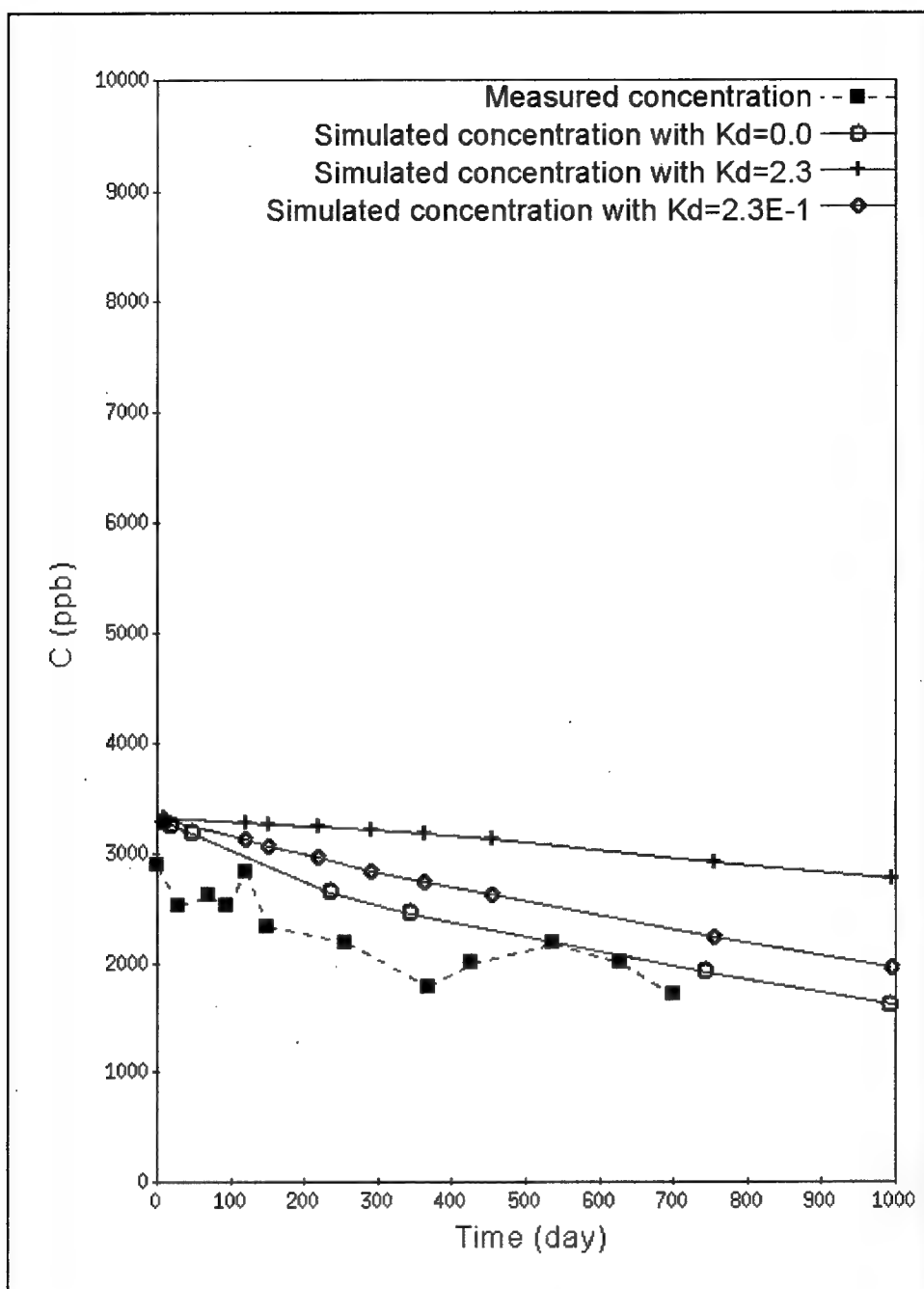


Figure D13. Time series of TNT concentration for measured and calibrated model with different adsorption coefficients (L/kg) as shown above (Original data were from MW083U)

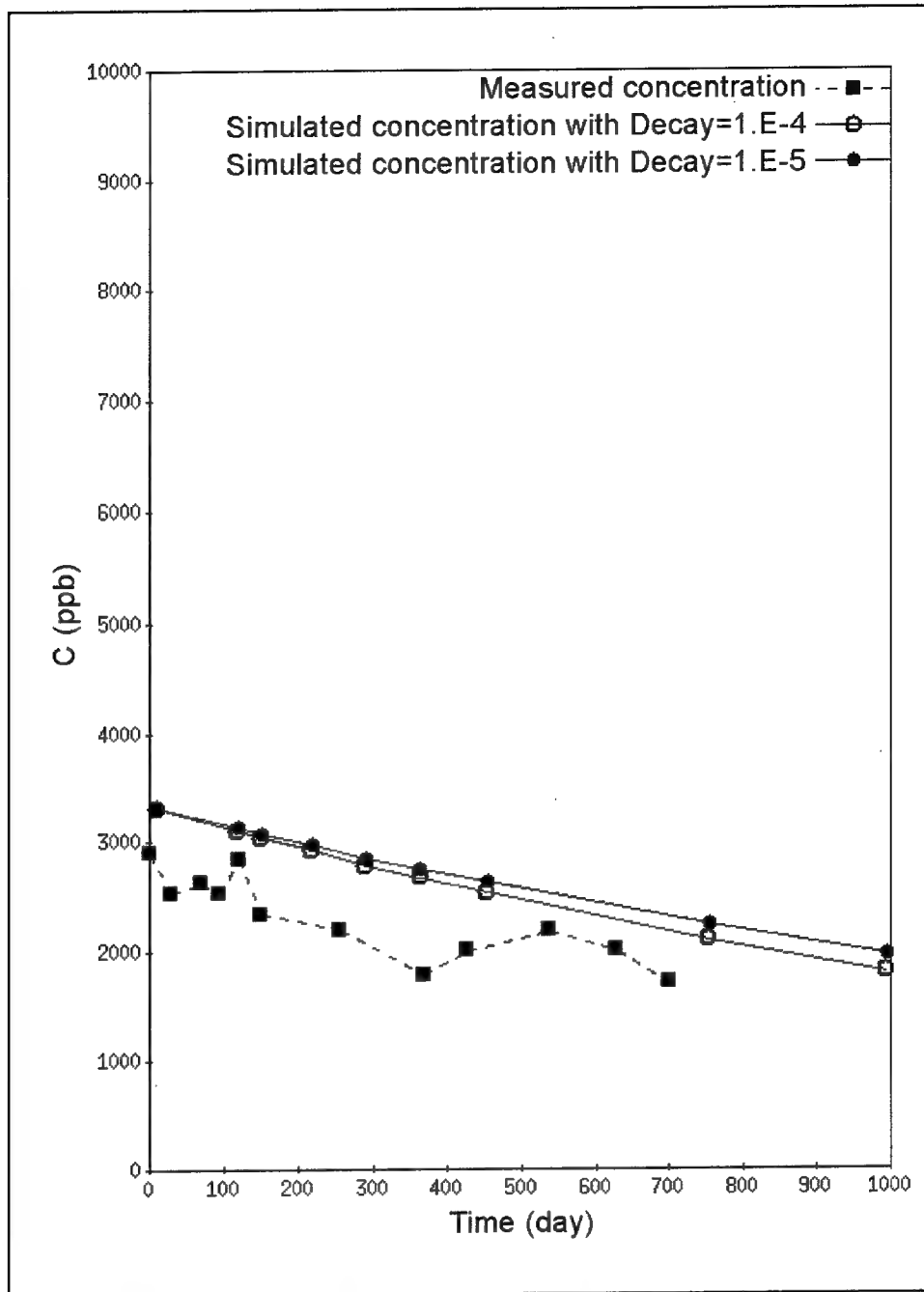


Figure D14. Time series of TNT concentration for measured and calibrated model with different first-order decay rates (1.E-4 and 1.E-5 L/day) and fixed adsorption coefficient of 2.3E-1 L/kg as show above (Original data were from MW083U)



## Predictive Simulations

Prediction of the fate and transport of TNT and RDX at the LAAP site requires calculating future flow and transport patterns derived from available historical data. The future boundary and other required model conditions are a mathematical statement of specific hypotheses, based on past experiences.

To predict changes that might occur in the distribution of TNT and RDX at the site for a 20-year time interval, several assumptions were imposed on the model: (a) no additional source of contamination is added into the site; (b) infiltration rate stays constant throughout the time period under investigation; (c) flow boundary conditions recur every year; (d) no recharge or discharge through pumping occurs during the simulations. Adsorption coefficient of 0.23 and 0.3 L/kg and degradation rates of  $10^{-7} \text{ day}^{-1}$  and  $8.13 \times 10^{-6} \text{ day}^{-1}$  were used to develop a 20-year prediction of the fate and transport of TNT and RDX at LAAP, respectively.

When initial conditions (Figures D15 and D17 for TNT and RDX, respectively) are compared with simulations for 20 years (Figures D18 and D20 for TNT and RDX, respectively), the areal extent of both plumes is diminishing. The highest concentration is reduced from 10,500 to 250  $\mu\text{g L}^{-1}$  for TNT and 23,200 to 620  $\mu\text{g L}^{-1}$  for RDX. The predicted results should be updated, adjusted, and verified as new data become available. For example of the iterative way in which a model prediction can be improved as new information is obtained, the reader is referred to Jorgensen (1981).

## Contaminant Mass

One of the three lines of evidence for natural attenuation (EPA 1977b) is to demonstrate reduction of contaminant mass over time. Contaminant masses were calculated using the measured and predicted TNT and RDX concentrations along with iso-surface volume calculation of GMS (1996). The estimated initial (February 1996) masses of TNT and RDX were 51.97 and 77.74 metric tons, respectively. The masses estimated at the end of the 2-year monitoring were 49.87 and 68.04 for TNT and RDX, respectively. The predicted values after 20 years are 7 and 4 metric tons for TNT and RDX, respectively. The accuracy of these numbers is controlled by the assumptions and limitation of FEMWATER and iso-surface calculations of GMS.

## Conclusions

GMS provided efficient numerical tools to integrate and analyze complex and multidisciplinary field data into simpler graphic forms that were used to illustrate fate and transport of contaminant plumes. The measured and simulated flow data indicated slow subsurface flow at the LAAP site, due to the low permeability media and low hydraulic gradients. The TNT and RDX plumes are



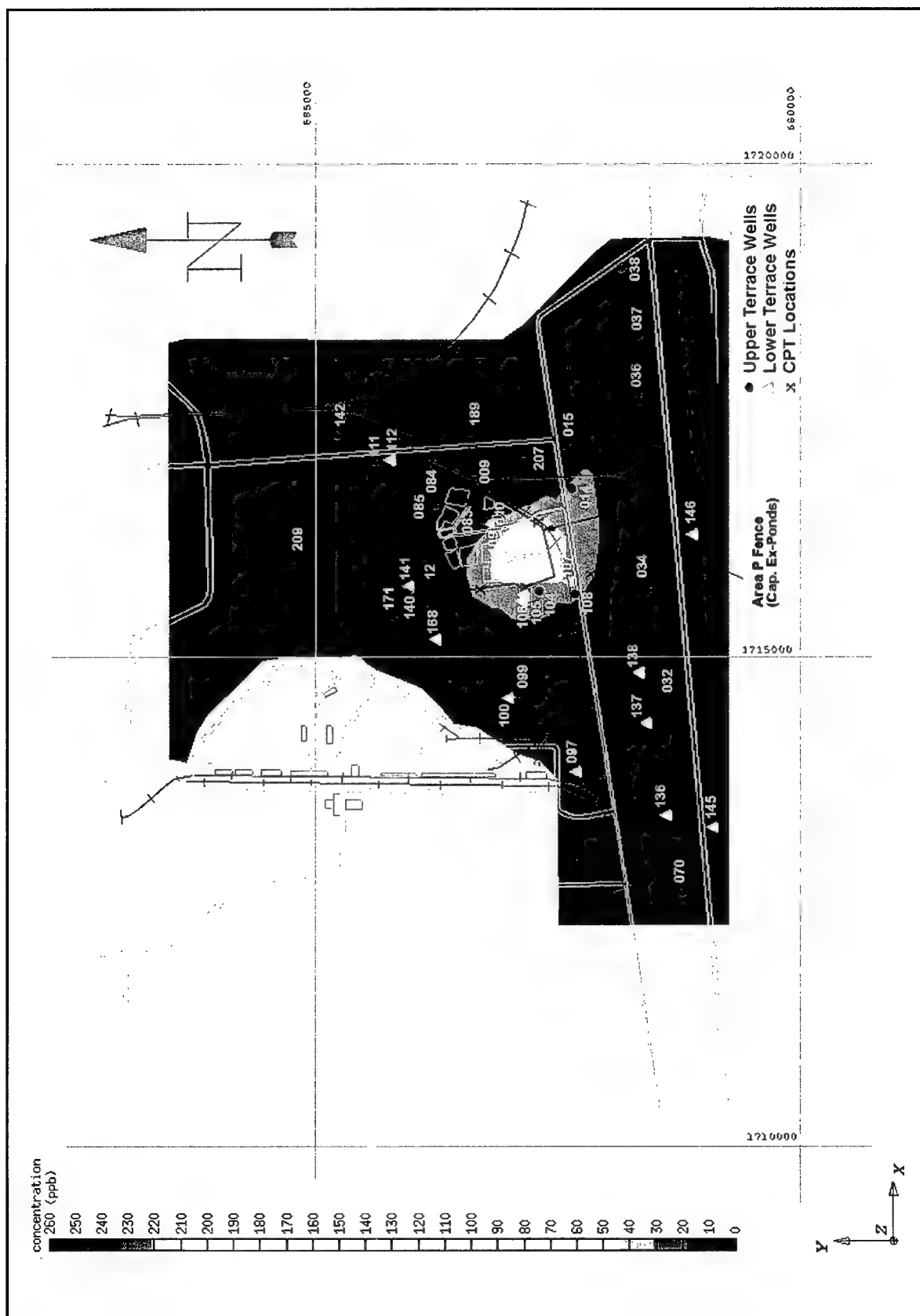


Figure D16. Predicted distribution of TNT plume after 20 years



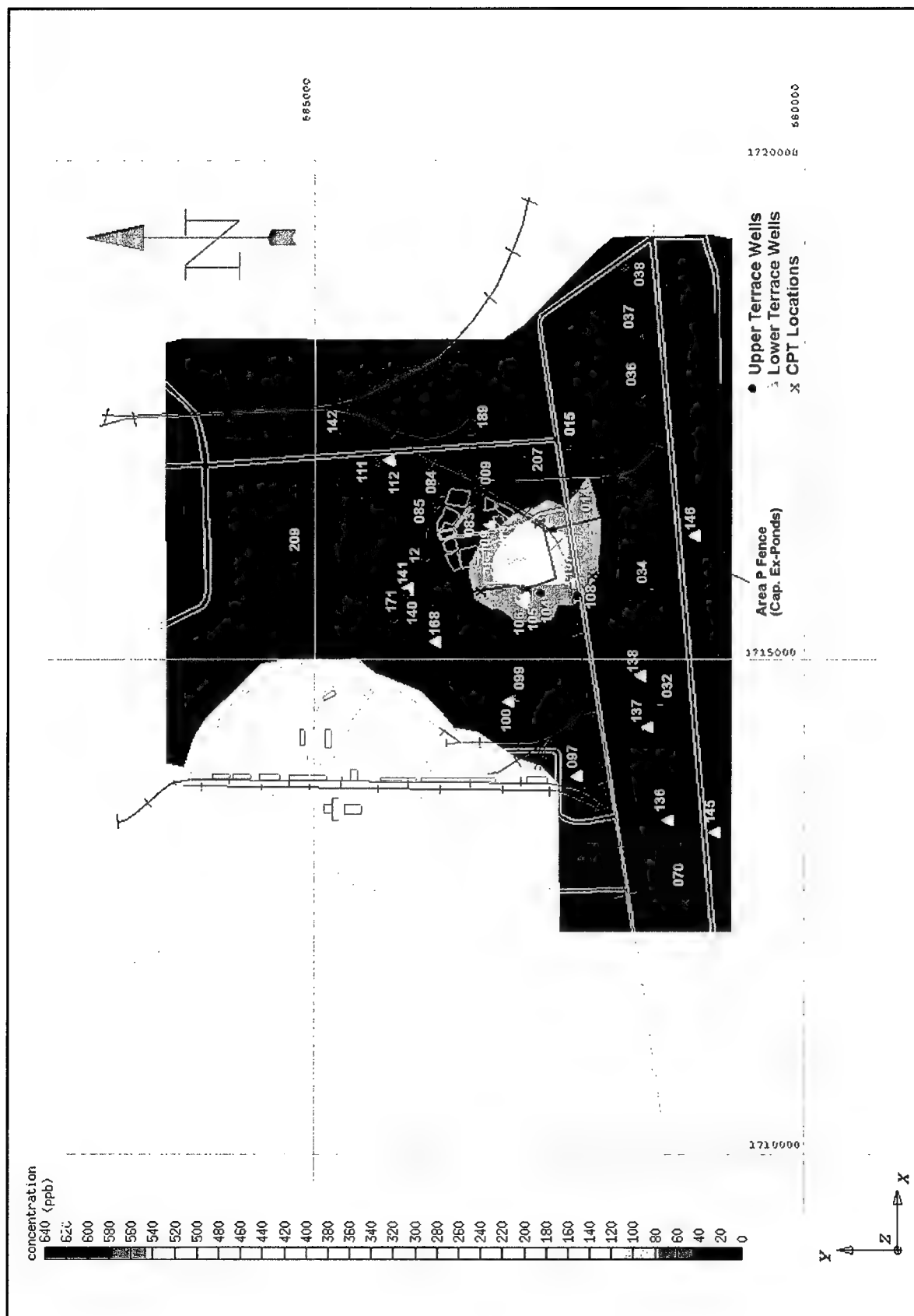


Figure D18. Predicted distribution of RDX concentration after 20 years

virtually static. The simulated flow directions are consistent with the direction of explosives plume propagation. Although some of the contaminant may move from the Upper Terrace Aquifer to the Lower Terrace Aquifer, the total mass of contaminants are anticipated to decline.

The simulated results indicated that explosives at LAAP may be reduced naturally without posing any threat to offsite receptors. The supporting factors for natural attenuation of explosives at the site including low degree of sorption, low values of the hydraulic conductivity, and low rate of mineralization were evaluated and illustrated. Even though the reduction process is very slow, the plume is confined to a limited area and is not moving significantly. The results of contaminant mass calculations indicated that the initial mass of TNT and RDX will be reduced significantly during 20 years of the simulations. The sensitivity analysis suggested that the important model input parameters are the adsorption coefficient rates and the biodecay rates. The predicted results should be adjusted and the calibration processes repeated as new data become available.

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## List of Symbols

$\theta$  = Moisture content, dimensionless

$\theta_r$  = Residual moisture content, dimensionless

$\phi$  = Porosity, dimensionless

$h$  = Pressure head, L

$h_b$  = Bubbling or air-entry pressure, L

$\delta$  = Kronecker delta tensor

$\kappa$  = Decay rate constant (1/T)

$\lambda$  = Pore size distribution, dimensionless

$Kr$  = Relative hydraulic conductivity, dimensionless

$C_m(h)$  = Water content, dimensionless

$\theta_w$  = Moisture content, dimensionless

$C$  = Aqueous phase concentration, M/L<sup>3</sup>

$t$  = Time, T

$\rho_b$  = Bulk density of the medium, M/L<sup>3</sup>

$S$  = Solid, or adsorbed phase concentration, M/M

$V$  = Flow velocity, L/T

$\nabla$  = Del operator

$D$  = Dispersion coefficient tensor, L<sup>2</sup>/T

$Q$  = Volume flow rate per unit volume of source or sink, 1/T

$C_{in}$  = Source or sink concentration, M/L<sup>3</sup>

$\rho^*$  = Density of injected fluid, M/L<sup>3</sup>

$\rho$  = Fluid density, M/L<sup>3</sup>

$\rho_0$  = Reference water density, M/L<sup>3</sup>



$K_d$  = Distribution coefficient,  $L^3/M$

$S_{max}$  = Maximum concentration allowed in the medium isotherm,  $M/M$

$K_L$ ,  $K_F$ ,  $n$  = Constant coefficients and power for Langmir and Freundlich isotherm, dimensionless

$\alpha_L$ ,  $\alpha_T$  = Longitudinal and lateral dispersivity coefficients,  $L$

$\alpha_m$  = Molecular diffusion coefficient,  $L^2/T$

$|V|$  = Magnitude of velocity,  $V$ ,  $L/T$

$\delta$  = Kronecker delta tensor, dimensionless

$\tau$  = Tortuosity, dimensionless

$R$  = Retardation coefficient, dimensionless

$u$  = Mean water velocity,  $L/T$

$u_s$  = Mean chemical (solute) velocity,  $L/T$

$C_{total}$  = Total concentration,  $M/L^3$

$C_w$  = Concentration of chemical in liquid phase,  $M/L^3$

$C_s$  = Concentration of chemical adsorbed to solid particles,  $M/L^3$

$Sw$  = Moisture content, volume of water/bulk

# Appendix E

## Statistics

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The primary statistical property of a parameter or data value is the distribution function, also referred to as the probability or density function. The distribution function is the mathematical functional relationship between the value of a parameter or data point and the frequency of occurrence of that value or data point. Typically, the easiest distribution to understand is a bell-shaped curve also referred to as Gaussian, or normal, distribution; however, such distributions seldom occur with environmental data. A distribution commonly approximated by environmental values is the lognormal distribution. Certain quantified parameters that express properties of the distribution can be used to assess data on which decisions will be based. The most important and commonly used properties of the distribution function relate to the central location, variation (or spread), and asymmetry of the distribution. Some of the basic measures of the distribution include the following:

- *Mean* - a measure of the central location within the distribution. If the distribution is bell-shaped (or normal), then the mean is the arithmetic average of the values. If the distribution is lognormal, then the mean (known as the geometric mean) is calculated as the average of the logarithms.
- *Median* - also a measure of central location or 50th percentile of the distribution. For a set of values arranged in numerical order, the median is the middle measurement. For example, for a set of values 2, 3, 3, 4, 5, 5, 6, 6, 7, 7, 7, 9, the median is 5.5 (the arithmetic mean is 5.3).
- *Mode* - the value with the maximum frequency of occurrence. Given the numbers presented in the definition of the median, the mode is 7.
- *Variance or Standard Deviation* - a measure of the variability or spread of values around the mean value. Mathematically, the units of variance are the square of the measurement unit, which can sometimes be inconvenient or not appropriate for the problem at hand. Therefore, the square root of the variance is used, which is referred to as the standard deviation.

- *Range* - the difference between the largest and smallest values of a set of values. From the numbers presented in the definition of the median, the range is 7.
- *Standard Error of the Mean* - a measure of the accuracy to which the mean has been determined by the data set. The standard error is the standard deviation of the sampling distribution of the mean and is calculated by dividing the sample standard deviation by the square root of the sample size.
- *Confidence Interval* - the interval in which a population parameter is determined to lie with a specified degree of confidence or level of probability. Given a 95-percent confidence interval for the mean, in repeated sets of samples of the same size from the same distribution, 95-percent of the calculated intervals are expected to contain the true population mean. *Confidence Limits* are the two boundary points of the confidence interval and are usually calculated as the sample mean plus or minus the quantity (standard error of the mean times the appropriate percentile of the Student's *t* distribution).
- *Prediction Interval* - the interval in which an individual response is predicted to lie with a specified degree of confidence or level of probability. The prediction interval for an individual response will be broader than the corresponding confidence interval for the average (mean) response.
- *Parametric (or Distribution-Dependent) Statistical Tests* - tests that assume that the data are sampled from a specified type of population distribution, usually the normal or lognormal distribution. Commonly performed parametric tests include the two-sample *t*-test, analysis of variance, and Pearson's correlation.
- *Nonparametric (Distribution-Free or Ranks-Based) Statistical Tests* - tests that make no assumption about the specific form of the underlying population distribution. Such tests are often performed on the ranks of the sample data rather than the raw data and include the two-sample Wilcoxon rank-sum test, the Kruskal-Wallis one-way analysis of variance by ranks, and Spearman's rank correlation.

Several other statistical parameters and methods of evaluating uncertainties exist. Numerous texts are available on this subject (e.g., Gibbon 1994 and Gilbert 1986). Of primary importance in the statistical evaluation is understanding and communicating the impacts that the results of the statistical analysis have on any calculations and decisions based on those calculations.

# **Appendix F**

## **Interim Army Policy on Natural Attenuation for Environmental Restoration**

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DEPARTMENT OF THE ARMY  
ASSISTANT CHIEF OF STAFF FOR INSTALLATION MANAGEMENT  
600 ARMY PENTAGON  
WASHINGTON DC 20310-0600

DAIM-ED-R (200-1c) 12 SEP 1995

MEMORANDUM FOR SEE DISTRIBUTION

SUBJECT: Interim Army Policy on Natural Attenuation for Environmental Restoration

1. This memorandum provides interim policy for requiring the consideration of natural attenuation as a remedial action alternative for installation restoration activities under the authorities of Comprehensive Environmental Response, Compensation, and Liability Act Superfund Amendments and authorization Act of 1986, Resource Conservation and Recovery Act, Underground Storage Tanks, National Environmental Policy Act, or relevant State and local regulations. This policy should be implemented immediately for decision documents or Records or Decision resulting from Army's environmental actions.

2. While natural attenuation has no specific regulatory definition, the U.S. Army defines natural attenuation as the reduction of contaminant concentrations in the environment through biological processes (aerobic and anaerobic biodegradation, plant and animal uptake), physical phenomena (advection, dispersion, dilution, diffusion, volatilization, sorption/desorption), and chemical reactions (ion exchange, complexation, abiotic transformation). Terms such as

intrinsic remediation or bio-transformation are included within the more general natural attenuation definition.

3. Natural attenuation is not a no-further-action alternative. Natural attenuation typically requires extensive monitoring to ensure that the predicted natural processes are taking place. Natural attenuation remedies might take longer than engineered remedies to correct the problem. Additionally, there should be a readily available contingent remedy for the site. It will take credible scientific data, site characterization data, and predictive modeling to prove that natural processes are sufficient to reduce risk in the time frame required. The Army will need that proof to ensure acceptability of the natural attenuation remedy.

4. The Army is presently not giving full consideration to natural attenuation as a potential remedy for environmental contamination. Therefore, it is Army policy that natural attenuation must be considered as a candidate remedy for contaminated sites either alone or in combination with active engineered measures. An engineered remedial action will not be approved unless data exists to prove that natural attenuation is inappropriate for a site cleanup.

5. Full protocols on the use of natural attenuation for different classes of contaminants commonly found at Army bases are presently under development at the US Army Environmental Center (USAEC). Until these protocols are available, use of the Air Force Center for Environmental Excellence's protocol (Technical Protocol for Implementing the Intrinsic Remediation (Natural Attenuation) with Long-term Monitoring Option for Dissolved-Phase-Fuel Contamination in Ground Water) for petroleum contaminants is recommended. Questions concerning other media/contaminants should be addressed to Mr. Ira May, POC at USAEC, (SFIM-AEC-IRG), Comm (410) 671-1522, DSN 584-1522 or FAX (410) 671-1548.

6. The Office, Director of Environmental Programs POC is Mr. Michael Vogt, (DAIM-ED-R), Comm (703) 693-4635, DSN 223-4635 or FAX (703) 697-0338.

FOR THE ASSISTANT CHIEF OF STAFF FOR INSTALLATION  
MANAGEMENT:

/signed/  
FRANK R. FINCH, P.E.  
Colonel, GS  
Director, Environmental Programs

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